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Treatment of Regulated Discharges from Shipyards and Drydocks

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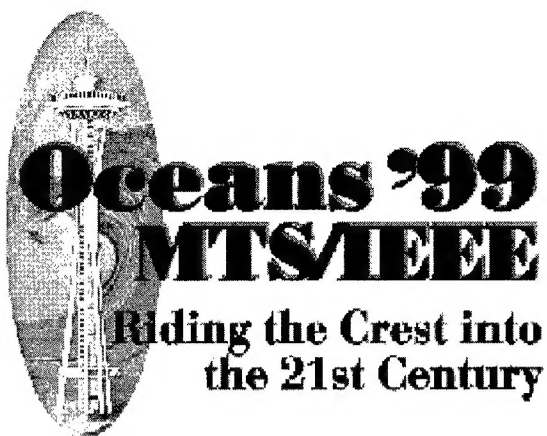
Proceedings of the Special Sessions held at Oceans '99 in Seattle, Washington, Sept 13-16, 1999 on:

"Treatment of Regulated Discharges from Shipyards and Drydocks"

Michael A. Champ, Thomas J. Fox, and Alan J. Mearns
Proceedings Volume Editors

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PREFACE

Summary of Seattle Oceans '99
Treatment of Discharges from Shipyards Panel Discussion

A closing panel discussion was scheduled for review and discussion of the papers presented by speakers at the special sessions. Participants in the panel discussion were: Stewart Evans (University of Newcastle, UK), Mike Pursley (MARAD), Joel Salter (USEPA OW), Chris Swanson (Miller Associates, CQD), Alan Mearns (NOAA, HAZMAT) and Mike Champ (ATRP Corporation). Tom Fox was unable to participate in the panel discussion, because he was previously scheduled for his daughters wedding.

The papers in this volume represent an excellent global update and state-of-the-art on the treatment of discharges from shipyards. Several papers in these Proceedings were not presented by the authors themselves, but were presented by American colleagues in attendance at the conference. Several others have been added as we learned of overseas studies and projects following Oceans '99. We wanted to publish a bibliography in this area, but have found only a sparse number of technical publications. We have ensured that most of these were referenced in this volume. Thus, the papers in this volume represent more of a global collection of the available technical literature than just those presented at the Conference. We also added the TBT Special Sessions papers to this volume, both because of their relevance and unavailability for publication with the regular Conference Proceedings.

The panel discussion, evolved into a working group from the floor of the session representing the participants on the last day of the conference. This ensured better balance and greater diversity of discussion, since half of the panel members were not speakers, but attendees.

The panel identified a series of major concerns or issues from the presented papers which, in turn, became recommendations for further consideration by any interested parties: governments (local, regional or national), the shipping industry, the shipyard industry, port and harbor authorities or non-government organizations and environmental organizations. The following is a summary of the recommendations of speakers and panel participants at the Ocean's '99 Conference.

SUMMARY AND RECOMMENDATIONS

Review of the Science Associated with the Regulation of TBT

- With regard to the peer review of the science being used in the international regulatory decision process at the International Maritime Organization (IMO), it was felt that the trend data presented for the regulated countries did not warrant at this time a global ban. However, global implementation of national regulations with necessary modifications (to meet existing environmental conditions in enclosed ports or harbors) is recommended given the trade offs to the shipping industry of increased annual costs ranging from $ 500 million to $ 2 billion.

- Either cooperation from existing international scientific advisory organizations or the formation of a new - special group to assist and complement the international regulatory and global decision-making processes at IMO.

Policing After Implementation of the Global Ban for TBT

- There is no non-destructive and/or inexpensive rapid method available for detecting and measuring TBT on a ship's hull after the ban is implemented.

- There is no neutral-third party-independent certification process for ship owners that is accepted as proof that their ship hulls are TBT paint free.

- There is no national or international policing system to enforce the TBT ban, or punish those that are in violation.

Removal and Disposal to TBT from Ships Hulls (2001-2008)

- There is only one advanced waste treatment system in the world that has successfully treated industrial volumes of TBT in wastewaters in accordance with shipyard operations (36 hours for washdown). The CASRM Barge Mounted System has evolved from bench type laboratory scale treatment systems to a shipyard size demonstration project.

- There is no inexpensive advanced waste treatment system or technologies available in commercial sizes that can rapidly treat million gallon quantities of TBT contaminated ship washdown or runoff wastewaters from shipyards and drydocks.

- There are no federal, industry, and/or internationally funded organizations to promote the development and/or evaluation (including certification) of advanced waste treatment technologies to treat TBT discharges from shipyards.

Promotion and Development of Alternatives to the Use of TBT

- Except for promotion by IMO, there are no federal, industry, and/or internationally funded organizations to support and fund the R&D for TBT alternatives in the marketplace.

- There are no international standard protocols or tests that can be used to assess, compare and evaluate available alternatives to TBT antifouling paints.

- There are no federal, industry, and/or internationally funded international organizations to test, evaluate, and certify available alternatives to TBT antifouling paints. The recently proposed International Marine Coatings Board (see Champ, 1998 and 1999a citations in this volume) was discussed and endorsed by the panel.

BACKGROUND

The IMO Marine Environment Protection Committee (MEPC) recommended in November 1999 that IMO, should hold a Conference in the 2000-2001 biennium to adopt a legal instrument (global treaty) to regulate the use of shipboard anti-fouling systems, in particular to phase out those containing organotins such as tributyltin (TBT). TBT paint is used to prevent the growth of marine organisms, such as barnacles, on the hulls of ships. TBT based paints are the most effective antifouling paints known. They are designed to work by continuously leaching TBT from the coating into the surface layer of water surrounding the hull. It is estimated that over 70% of the 27,000 vessel global merchant fleet is currently coated with TBT antifouling paints.

TBT is known to be extremely toxic to some marine animals. Adverse effects have been documented at concentration levels of ng/L (parts per trillion) such as shell abnormal growth deformities in oysters and imposex (sex change) in dogwhelks. Concern about the toxicity of TBT led the U.S. Congress to pass the *Organotin Paint Control Act in 1988*. Similar legislation was passed in other major maritime countries. Continued concern has led the United States to support an international ban on the use of TBT in conjunction with other nations at IMO.

Tens of thousands of port calls are made each year at U.S. ports, by ships coated with TBT paint, leaching TBT into waterways and sediments. Unfortunately, the global ban will be toothless, because at this time there are no non-destructive methods available to port and regulatory authorities to detect or measure TBT on ship hulls visiting U.S. ports or coastal waters. Absence of this technology presents problems for enforcement of the proposed ban, because large ocean-going commercial ships can be painted in shipyards in any country of the world. The current (destructive) methods for the analysis of TBT are both time-consuming (1-2 days) and expensive ($ 500-1000/per sample).

Between 2003 and 2008, approximately 20,000 ships in global commerce today will have to be scraped to bare metal removing more TBT than in the last 40 years combined. Normally when a ship goes into the shipyard for cleaning and repainting, if it is painted with TBT, a high pressure power wash can be used to remove just the top or damaged layer(s) keeping the remaining base coats. Following the global treaty to ban the use of TBT by the International Maritime Organization (IMO) and the mandatory removal of TBT from all ships, shipyards will be faced with a major dilemma. They will have to treat large quantities of TBT wastewater as a toxic waste.

To protect the marine environment from discharges of TBT, shipyards all over the world need a new and inexpensive process to treat TBT wastewater. A project funded by the U.S. EPA and the State of Virginia has demonstrated barge mounted system technologies that can TBT remove from shipyard wastewaters to below 50 ng/L using Granular Activated Carbon (GAC) columns (Fox et al., this volume). While this method is technically effective, it is not very cost effective, because the life of the GAC columns is reduced by the high levels of dissolved organic compounds naturally present in the shipyard wastewaters.

In the U.S., the lack of an advanced technology for ship yards to inexpensively remove TBT from wastewaters, could precipitate:

- Gross violations of State TBT Water Quality Standards, and discharge permit regulations for TBT (at present only the State of Virginia has a VPDES discharge permit level of 50 ng/l); and/or
- A significant reduction of work in U.S. shipyards (which are currently a depressed business) as they loose a large volume of ship repair and repainting business over the next 10 years.

OBJECTIVES OF THE SPECIAL SESSIONS AND PROCEEDINGS

The objectives of the special sessions on the Treatment of Regulated Discharges from Shipyards and Drydocks and Organotin (TBT) at the Oceans '99 Meeting in Seattle have been to:

- Characterize waste waters from different types of shipyards, drydocks, operations (etc.);
- Review and evaluate wastewater treatment technologies currently used in shipyards;
- Promote technology transfer;
- Review policy and regulatory strategies;
- Discuss results of TBT studies and findings;
- Discuss available alternatives to TBT;
- Review R&D needs; and
- Publish in one-volume papers from the Special Sessions.

The data, information and literature associated with identifying and treating the wastewater discharges from shipyards and drydocks is mostly unpublished in the technical literature and not very available. These data can be in very gray and unpublished shipyard regulatory databases or data files or summary water quality regulatory monthly compliance records. Such data files are kept by individual shipyards for review by regulatory officials and are never published. If this data were collected for compliance purposes, there could be a summary of tabulated or plotted data. If discharge data and information were collected as part of a R&D Project, there may be a technical report available (application or cleaning costs, or evaluation of application or cleaning technologies, etc.).

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SIMULATION OF STORMWATER RUNOFF FROM MARINE DRYDOCKS

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and Laura J. Harrell[4]

Abstract

Stormwater runoff from a floating marine drydock can be a major source of pollution for the waterway in which the drydock is located. Significant amounts of pollutants build up over drydock surface due to intensive industrial activity. During periods of rainfall these pollutants can be washed off and quickly transported into the receiving water. A mathematical model has been developed in this study to simulate the quantity and quality of stormwatwer runoff from marine drydocks. The mathematical model is based on the two-dimensional kinematic-wave and convective transport equations for total suspended solids. An empirical formula is used to model the wash-off process. An implicit finite difference scheme is employed to solve the governing equations of the model numerically. Also, the quantity and quality of stormwater runoff from a private drydock has been monitored under actual rainfall conditions. The samples collected were analyzed in the laboratory to determine the pollutant loadings of the runoff. This data was used to test and verify the mathematical model.

Keywords: Drydock, Stormwater, Runoff, Pollutant, Total Suspended Solids, Kinematic-wave

INTRODUCTION

Discharges from non-point sources such as agricultural and urban stormwater runoff have recently been recognized as major causes of pollution of surface waters. Contaminants from motor vehicles, construction activities, chemicals used in agriculture, atmospheric fallout, animal feces, solid waste litter and other anthropogenic sources build up on the land surface and may be mobilized by rainwater. Stormwater runoff from urban areas mobilizes substantial amounts of pollutants, and their origin can often not clearly be defined. In the past large scale studies have been conducted to investigate urban stormwater runoff. Interestingly, little attention has been

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paid to stormwater runoff from shipyard drydocks and its impact on the adjacent waters in the recent literature, although water pollution is a serious problem in coastal areas (U.S.E.P.A., 1996).

Shipyard (floating) drydocks are sites of intensive industrial activity in the construction, repair, and maintenance of ships. Because of the location of floating drydocks in a waterway and their regular submersion below the water surface, materials located on the surface of a drydock can potentially be washed into the surface water by solubilization or transport in particulate form. While shipyards are careful to clean drydock surfaces prior to submersion, there is the potential for wash-off of materials from the drydock surface during periods of rainfall. Runoff is generally quickly generated because the drydock surface is impermeable and the runoff volume can be significant given the area of drydocks can exceed several acres.

The potential sources of pollutants in the stormwater runoff are strongly dependent on the activities performed on a drydock. Removing and applying paint to a ship's hull is an important and common drydock activity that can lead to the accumulation of toxic metals on a drydock surface. The construction of new ships and repair of older vessels both require extensive preparation of steel surfaces and abrasive (grit) blasting is a widely used method to pretreat a ship superstructure. It basically involves the impingement of grit with high-pressure air to remove paint, rust, and contaminant materials that adhere to the surface. Other methods for surface preparation include pressure washing and hydroblasting before metal primers and antifoulants are applied.

Both spent blasting grit and marine paints contain toxic materials, which may reach the receiving water. During the period before a storm event airborne particles from stack gases and exhaust fumes may also build up on the drydock surface and some contaminants can also originate from motor vehicles and other machinery operated on the drydock. The prediction of pollutants in stormwater runoff from drydocks, especially heavy metals, requires knowledge of the composition of the materials used during ship maintenance, the pattern of accumulation on the drydock surface, and the mechanism of mobilization during a rainfall event.

Like other major industries, shipyards have to comply with local and federal toxic effluent limitations, as required by the National Pollutant Discharge Elimination System (NPDES). Although the toxicity of effluents from drydocks is being assessed for compliance purposes, little research has been conducted to investigate the composition and transport mechanisms of pollutants in runoff from shipyard drydocks. The chemical and physical processes which control the fate and transport of trace metals in rainfall runoff from drydocks need to be examined in order to develop effective measures to prevent negative impacts on the receiving water.

As part of a comprehensive study of drydock runoff a mathematical model was developed that can be used to simulate the runoff quantity and quality from a shipyard drydock. Hydrological and water quality data were collected from a private drydock during several rain events and were used to verify the mathematical model. The total suspended solids concentration was chosen as a representative parameter to characterize the quality of the drydock runoff in the mathematical model, because it is believed that toxic metals (i.e. copper and lead) are mobilized in proportion to the overall particulate matter (Pommerenk, 1996).

DESCRIPTION OF THE MATHEMATICAL MODEL

The stormwater runoff model consists of two components. The first component is for modeling the surface runoff rates from a drydock. The second component is for modeling the washoff and transport of particulate pollutants by the surface runoff.

Runoff Component

The runoff over the surface of a drydock during and following a rain event is represented by the two-dimensional kinematic-wave equations. The equation of continuity is written as

$$\frac{\partial y}{\partial t} + \frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = r \qquad (1)$$

where:

y	=	flow depth
t	=	time
q_x	=	flow rate in x-direction per unit width
q_y	=	flow rate in y-direction per unit width
x, y	=	flow directions
r	=	rate of rainfall

The momentum equations in the x and y directions are approximated by the respective kinematic relationships, as:

$$\frac{n^2 u_x \sqrt{u_x^2 + u_y^2}}{c_0^2 \, y^{4/3}} = S_x \qquad (2)$$

and:

$$\frac{n^2 u_y \sqrt{u_x^2 + u_y^2}}{c_0^2 \, y^{4/3}} = S_y \qquad (3)$$

where:

n	=	Manning roughness factor

$$c_0 \quad = \quad 1.49 \text{ ft}^{1/3}/\text{sec} = 1.0 \text{ m}^{1/3}/\text{sec}$$

$u_x \quad = \quad$ velocity in the x-direction

$u_y \quad = \quad$ velocity in the y-direction

$S_x \quad = \quad$ dock surface slope in x-direction

$S_y \quad = \quad$ dock surface slope in y-direction

Noting that:

$$q_x = y \; u_x \tag{4}$$

$$q_y = y \; u_y \tag{5}$$

Eqs. 2 and 3 can be manipulated mathematically to obtain

$$u_x = \alpha_x \; y^{2/3} \tag{6}$$

$$u_y = \alpha_y \; y^{2/3} \tag{7}$$

$$q_x = \alpha_x \; y^{5/3} \tag{8}$$

$$q_y = \alpha_y \; y^{5/3} \tag{9}$$

where:

$$\alpha_x = \frac{c_o}{n} \; \frac{S_x}{\left(S_x^2 + S_y^2 \right)^{1/4}} \tag{10}$$

and:

$$\alpha_y = \frac{c_0}{n} \; \frac{S_y}{\left(S_x^2 + S_y^2 \right)^{1/4}} \tag{11}$$

Substituting Eqs. 8 and 9 into Eq. 1, we obtain:

$$\frac{\partial y}{\partial t}+\frac{\partial}{\partial x}\left(\alpha_x\ y^{5/3}\right)+\frac{\partial}{\partial y}\left(\alpha_y\ y^{5/3}\right)=r \qquad (12)$$

Equation 12 describes the spatial and temporal variation of the flow depth, y, over the drydock surface. This is a nonlinear partial differential equation for which no analytical solutions are available. Therefore, a finite difference scheme is adopted to solve Eq. 12 numerically to find y at specified locations over the drydock and at specified times. Once the flow depth is found, Eqs. 6 to 9 are used to determine the velocities and flow rates. In the solution of Eq.12 the appropriate boundary conditions are incorporated by setting $\bullet_y$ or $\bullet_x$ equal to zero at the side walls.

Particulate Pollutant Transport

The transport capacity of the runoff over a drydock surface is evaluated using the Low (1989) formula. Govers (1993) evaluated the performance of a number of similar formulae and found that the Low formula was satisfactory. The formula is written for the general flow direction in any consistent unit system as

$$q_s=\frac{6.42}{\left(s-1\right)^{0.5}}\left(Y-Y_{cr}\right)D\ S^{0.6}u_s \qquad (13)$$

where:

q_s	=	solids discharge per unit width
s	=	$\bullet_s/\bullet$
Y	=	dimensionless shear stress = $\bullet/\bullet_s'D$
Y_{cr}	=	critical dimensionless shear stress = $\bullet_{cr}/\bullet_s'D$
D	=	grain diameter
S	=	average surface slope
u	=	resultant velocity
$\bullet_s$	=	density of particles
$\bullet$	=	density of water
$\bullet_s'$	=	submerged specific weight = g ($\bullet_s - \bullet$)

$$g \quad = \quad \text{gravitational acceleration}$$

$$\tau \quad = \quad \text{shear stress} = \bullet\ g\ y\ S$$

$$\tau_{cr} \quad = \quad \text{critical shear stress}$$

The Low formula is based on the rationale that the particulate pollutants are picked up from the surface due to the shear forces. To account for the impact of raindrops, an empirical formula is adopted in the model. Over a time increment of $\bullet\ t$, the particulate pollutant splash from an area $(\bullet\ x \bullet\ y)$ is

$$s_p = a_3\ r_0^{0.3}\left[\ a_1\ \Delta t\ r_0 + a_2\ \Delta t\ r_0\ \log\ (\ 43200\ r_0\ )\ \right]\frac{\Delta x\ \Delta y}{\Delta t} \tag{14}$$

where:

$$s_p \quad = \quad \text{splash (lbs/sec)}$$

$$r_0 \quad = \quad \text{rate of rainfall (ft/sec)}$$

$$\bullet\ t \quad = \quad \text{time increment (sec)}$$

$$a_1, a_2, a_3 \quad = \quad \text{empirical constants.}$$

$$\bullet\ x, \bullet\ y \quad = \quad \text{side lengths of reference area (ft)}$$

This formulation is based on the kinetic energy of raindrops, and it has the same form as the formula proposed by Bubenzer and Jones (1971) and used previously by Akan and Ezen (1982) successfully. The empirical constants used in this model are $a_1 = 7363$, $a_2 = 2661$, $a_3 = 0.00055$. Also, $\bullet\ _{cr} = 0.02$ lbs/ft^2.

Components of the solids discharge in the x- and y-directions are determined by distributing q_s and s_p according to the flow rates as

$$Q_{sx} = q_s\frac{q_x\ \Delta y}{\left(\ q_x^2 + q_y^2\ \right)^{1/2}} + \frac{s_p}{\left(\ 1 + \dfrac{q_y\ \Delta x}{q_x\ \Delta y}\ \right)} \tag{15}$$

and

$$Q_{sy} = q_s \frac{q_y \, \Delta x}{\left(q_x^2 + q_y^2\right)^{1/2}} + \frac{s_p}{\left(1 + \dfrac{q_x \, \Delta y}{q_y \, \Delta x}\right)} \tag{16}$$

where:

Q_{sx} =   solids discharge in the x-direction (lbs/sec) per length • y

Q_{sy} =   solids discharge in the y-direction (lbs/sec) per length • x

The average concentration, c_s, is determined as

$$c_s = \frac{\left[\left(\dfrac{Q_{sx}}{\Delta y}\right)^2 + \left(\dfrac{Q_{sy}}{\Delta x}\right)^2\right]^{1/2}}{\left(q_x^2 + q_y^2\right)^{1/2}} \tag{17}$$

The conservation of mass equation in now written as

$$\frac{\partial \left(c_s \, y\right)}{\partial t} + \frac{\partial \left(c_s \, q_x\right)}{\partial x} + \frac{\partial \left(c_s \, q_y\right)}{\partial y} = W_s \tag{18}$$

where W_s = mass of solids picked up by the flow per unit area per unit time. In Eq. 18, q_x and q_y are known from the solution of the flow equations, and c_s is known from Eqs. 15 to 17. We can therefore write Eq. 18 in finite difference form and solve it for W_s.

Positive values of W_s will represent particulate pollutant pick-up by the runoff, and the negative values represent deposition over the drydock surface. If W_s is positive, then we must have $W_s <$ (P_s/• t) for the formulation to be valid where P_s = mass of particular pollutant present on the drydock surface per unit area prior to the time period • t. If $W_s >$ (P_s / • t), the pollutant pick-up rate predicted by Eq. 18 can not be sustained. In that event the model sets $W_s = P_s$/• t and corrects the values of the pollutant concentration , c_s, by solving Eq. 18 in finite difference form for c_s. Obviously, it is possible to have $P_s = 0$.

Finite Difference Equations

Analytical solutions are not available for the governing equations of the mathematical model. Therefore, finite difference methods are used to solve these equations numerically.

With reference to the computational grid shown in Fig. 1, Eq. 12 is written for cell (i,j) in finite difference form as:

$$\frac{y_{i,j} - y^o_{i,j}}{\Delta t} + \frac{\left(\alpha_x \, y_i^{5/3} \right)_{i,j} - \left(\alpha_x \, y^{5/3} \right)_{i-1,j}}{\Delta x} + \frac{\left(\alpha_y \, y^{5/3} \right)_{i,j} - \left(\alpha_y \, y^{5/3} \right)_{i,j-1}}{\Delta y} = r \qquad (19)$$

where:

- t   =   time increment

- x, • y   =   side lengths of a computational cell

   y   =   depth sought at the end of time period • t

   y^o =   known depth at the beginning of time period • t.
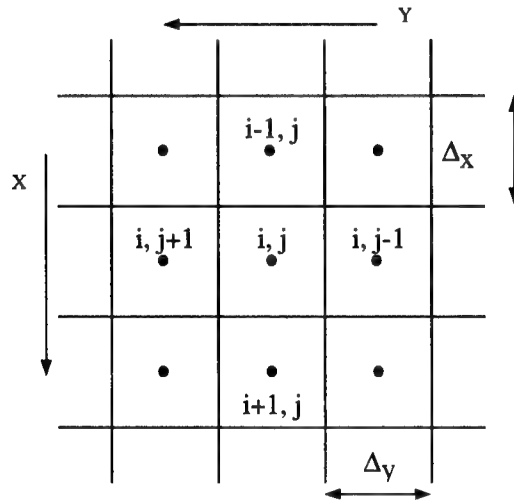
Figure 1. Finite Difference Grid for the Drydock.

For any time step of computation, Eq. 19 is written for each of the (NCOL x NROW) cells where NCOL = total number of columns and NROW = total number of rows. This will result in (NCOL x NROW) simultaneous algebraic equations containing the same number of unknowns, $y_{i,j}$, with 1, 2, . . . , NROW and j = 1, 2, ... , NCOL. The y^o values are known from the initial conditions for the first time step. For the subsequent time steps, the y^o values will be known from the previous time step results.

Equation 19 is solved by using the Newton method for each cell starting on the first row with cell (1,1). Then the cells on the subsequent rows are considered. It should be pointed out that at the time a cell (i,j) is considered, the values of $y_{i-1,j}$ and $y_{i,j-1}$ are known either from the boundary conditions, or from the results of the calculations already completed for the other cells.

Therefore, in Eq. 19 the only unknown will be $y_{i,j}$. Once the flow depths are calculated in all the cells, the velocities and the flow rates are found using Eqs. 6 to 9.

The particulate pollutant transport equation is written in finite difference form as

$$\frac{(c_s\, y\,)_{i,j}-(c_s\, y\,)^0_{i,j}}{\Delta t}+\frac{(c_s\, q_x\,)_{i,j}-(c_s\, q_x\,)_{i-1,j}}{\Delta x}+\frac{(c_s\, q_y\,)_{i,j}-(c_s\, q_y\,)_{i,j-1}}{\Delta y}=(\,W_s\,)_{i,j} \quad (20)$$

In this equation c_s values are known from Eq. 17 and y, q_x, and q_y values are known from the results of the flow model. Therefore, W_s, can be calculated explicitly for each cell. However, as discussed previously, if W_s so calculated turns out to be greater than $P_s/\bullet$ t for a cell, we set $W_s = P_s\,/\bullet$ t for that cell. Then we solve Eq. 20 for c_s using the Newton method to recalculate the particulate pollutant concentrations in the flow.

MONITORING AND CHARACTERIZATION OF DRYDOCK RAINFALL RUNOFF

Rain-generated runoff was sampled at a private drydock in Norfolk, Virginia. The drydock was a floating drydock, 950 feet in length, 192 feet wide with an impervious steel deck and approximately 40 feet high wing walls at the starboard and port sides as displayed in Fig 2. The deck is sloped from the centerline to the wingwalls, and the drydock is generally inclined to cause runoff to flow to the stern.

Once in the drydock, the major activities on the ship include pressure washing, hydroblasting, sand (grit-) blasting, hull painting, and machine repair. To prevent the paint spray to be transported by winds off the drydock, tarps typically cover the top of the drydock, as shown in Fig. 2. Hay bales, placed as shown in Fig. 2, serve as a control measure to capture particulate matter, especially sandblasting grit, that might otherwise be washed into the river.

Equipment and Setup

Stormwater runoff from the port side of the drydock was collected in a flume, made from stainless steel, which was installed at the stern of the drydock. The flume consisted of a rectangular section, which was closed on one end, and a short, converging section welded to the other end, where the water discharged to the river as shown in Fig. 3. This structure not only served as a flow-through trough, from which samples were collected, but also as the *primary measuring device* for determining the water discharge rate to the river. The shape and dimensions of the flume conformed to an H-type flume (Grant, 1992). The depth-discharge relationship for this type of flume was programmed into the flowmeter to calculate the flow of water through the flume.
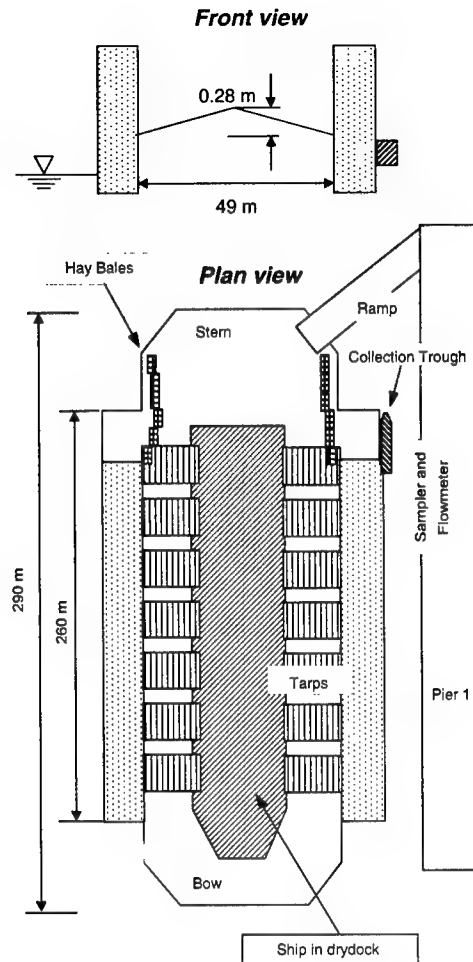
Figure 2. Drydock Schematic.

The automatic sampler contained 24 1000 mL polypropylene bottles in its air-tight base section. Rainfall at the drydock was measured with a tipping bucket rain gauge, which was mounted 30 yards away from the collection trough. The rain gauge was capable of measuring 0.01 - 22 inches of rain per hour and sent an electrical signal to the nearby flowmeter for every 0.01 inches of rain that the rain gauge received. The flowmeter was stored along with the auomatic sampler in a wooden box on the pier next to the collection trough and served the purposes of storing the rainfall data in two-minute time increments, measuring the water elevation in the trough and converting it to flow and storing the data in memory, and triggering the automatic sampler, if preset conditions were met. Upon triggering (turning on) by the flowmeter the sampler purged the vinyl suction line, which was submerged in the trough, and then pumped approximately one

liter of runoff into a sample bottle.
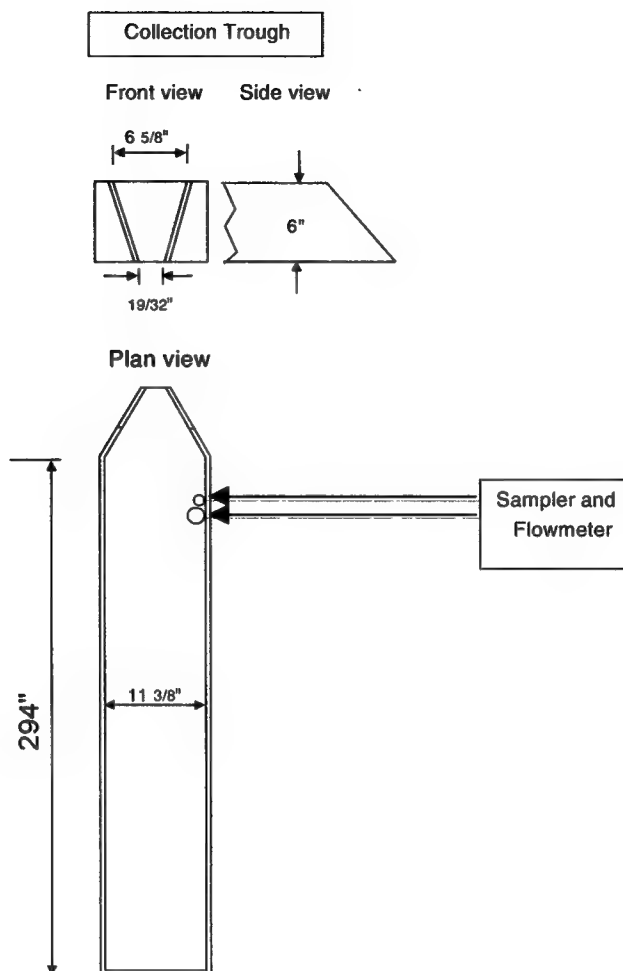
Figure 3. Collection Trough and Flow Measurement Location

The flowmeter was programmed to start the sampling sequence, when the following two conditions were met: The rainfall depth exceeded 0.01 inches within a 15 minute period, and the liquid level in the trough had to be greater than 0.5 inches. This ensured that the sampler was only triggered by rainfall and not by "runoff" from other sources; for example runoff generated by the drainage of ballast water from a ship in the drydock.

After the immediate collection of the first sample, the flowmeter triggered the automatic sampler to take one sample out of the trough for every 400 gallons of runoff, until either the 24 bottles were filled, or the sampling sequence was stopped manually, because the runoff event subsided

to negligible amounts. The flowmeter recorded the date and time each sample was collected so that the chemical characteristics of each sample could be compared to the time flow conditions during an event.

Laboratory Analyses

Total suspended solids concentrations were determined gravimetrically following APHA (1995) standard methods. Glass fiber filter disks were prewashed with deionized water and dried at 103°C for one hour. After cooling in a desiccator, the filter discs were transferred to clean aluminum weighing dishes and weighed on an electronic balance before analysis. A 20ml aliquot of the well-mixed sample was filtered using a vacuum filtration device. The filter disc was placed back into the weighing dish and dried at 103°C. The filtrate was transferred from the suction flask to another preweighed aluminum dish and also allowed to dry for 24 hours. After drying and cooling in a desiccator, the dishes were weighed and the total dissolved and total suspended solids concentrations were calculated as the difference in weight divided by the volume of sample.

VERIFICATION OF THE MODEL

The drydock stormwater runoff quantity and water quality data collected during four rainfall events were used in this study to verify the mathematical model. The absence of hay bayles blocking the runoff from the drydock during these events was the major factor for the selection of these events for verification purposes. When present, the hay bayles alter the hydraulics of the stormater runoff significantly invalidating the formulations used in the model. The four rainfall events used for verification are of November 7 and 11, 1995, and January 27 and March 1, 1996.

The computational grid used in the calibration runs is shown schematically in Fig. 4. This represents only one half of the drydock. Taking advantage of the symmetry, only one half of the drydock was investigated in this study. The computational grid consists of five columns and 38 rows. Each computational cell is 25 ft by 16 ft. The mathematical model calculates the flow depths and pollutant concentrations at the centroids of the cells. It also calculates the runoff and pollutant discharges entering and leaving the cells in the x- and y-directions. The lateral slope S_y is constant and is equal to 0.01146. The longitudinal slope, S_x, can vary, but it is normally set at 0.00267. The sampling station was at the edge of cell (34,5). Some of the cells are occupied by a ship. The total number of these cells depends on the size of the ship. Likewise, some of the cells are covered by tarps the extent of which can vary.

The waste load on the drydock deck is comprised of blasting grit, spent paint chips, and other debris. A sieve analysis was performed on a sample of spent blasting material. The sample was dried and sieved to separate size fractions. Then the density were found for each fraction (Fenn, 1996). This analysis resulted in a representative particle diameter of 0.0036 ft and a density of 6.2 slug/ft^3, which were used as input for calibration runs.
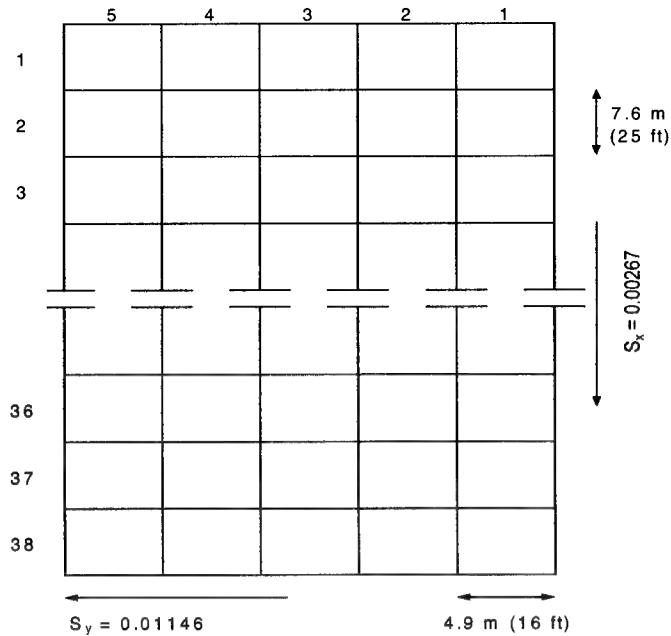
Figure 4. Computational Grid for Drydock.

Not all the model input variables were available for the verification runs. parameters. For instance the amount of rainfall intercepted and diverted by the tarps or a ship could not be determined directly. Therefore, these values were adjusted so that the measured and calculated total runoff would be nearly equal. Likewise, modeling the pollutant buid-up over a drydock surface was not part of this study, and the initial amount of pollutants available on a drydock prior to a rain event could not be measured directly. Therefore, the initial amounts were adjusted so that total amounts of measured and modeled TSS were nearly the same. Table 1 summarizes the conditions simulated in the model verification runs.

Table 1. Drydock Conditions for Model Simulations.

Date of Event		Nov. 7, 1995	Nov. 11,1995	Jan. 27, 1996	Mar. 1, 1996
Rain Duration [min]		500	120	264	556
Total Rainfall [in]		0.75	0.43	0.51	0.44
Tarp	Columns	N/A	N/A	1 to 5	1 to 5
	Rows	N/A	N/A	1 to 25	1 to 34
Ship Location	Columns	1 to 2	1 to 2	N/A	N/A
	Rows	1 to 34	1 to 25	N/A	N/A
Total Nonsoluble Solids Initially Available [lbs]		40	5.5	10	3.6
Rain Intercepted by Tarps %		N/A	N/A	43	43
Rain Intercepted by Ship %		80	55	N/A	N/A

Figure 5 displays a comparison of modeled and measured values of cumulative stormwater runoff rates from the drydock. Likewise, Fig. 6 displays a comparison of modeled and measured cumulative TSS discharge. The agreement appears to be reasonably good. Obviously, without measured values of the amount of the rainfall intercepted by the tarps and the initial distribution of pollutants over the drydock, the model can not be fully verified. However, the agreement between the measured and modeled values are encouraging.
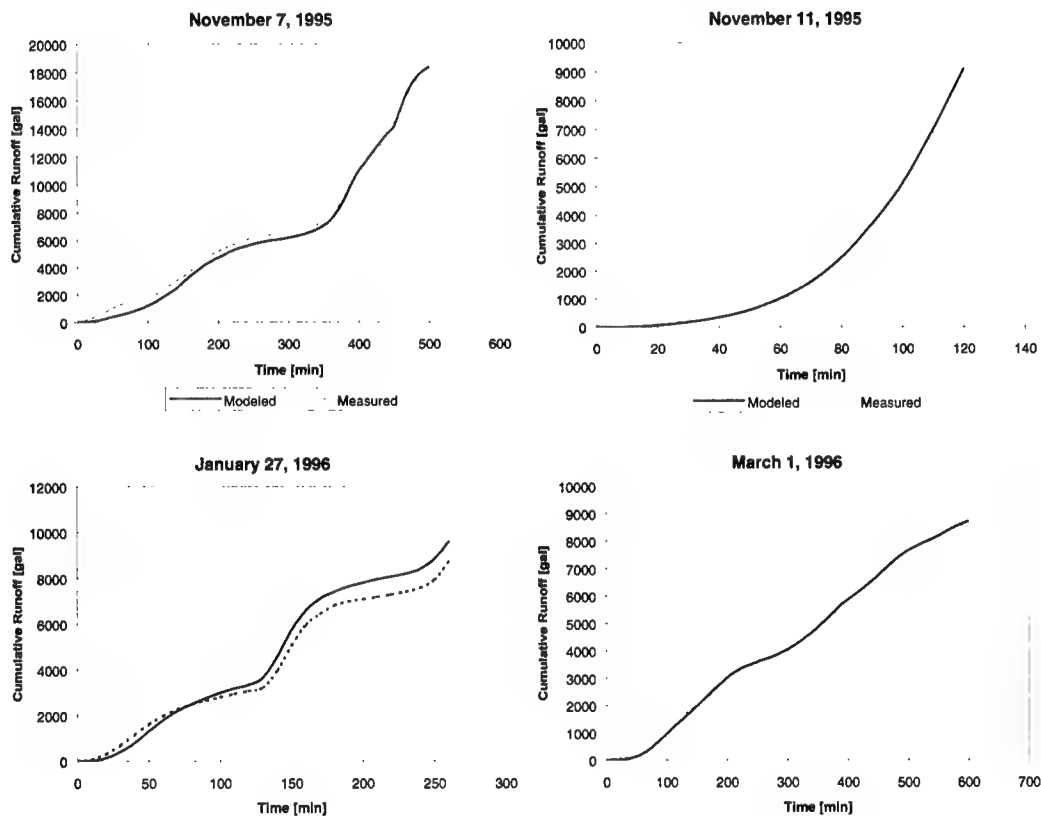
Figure 5. Modeled and Measured Cumulative Runoff for the Indicated Storm Events.
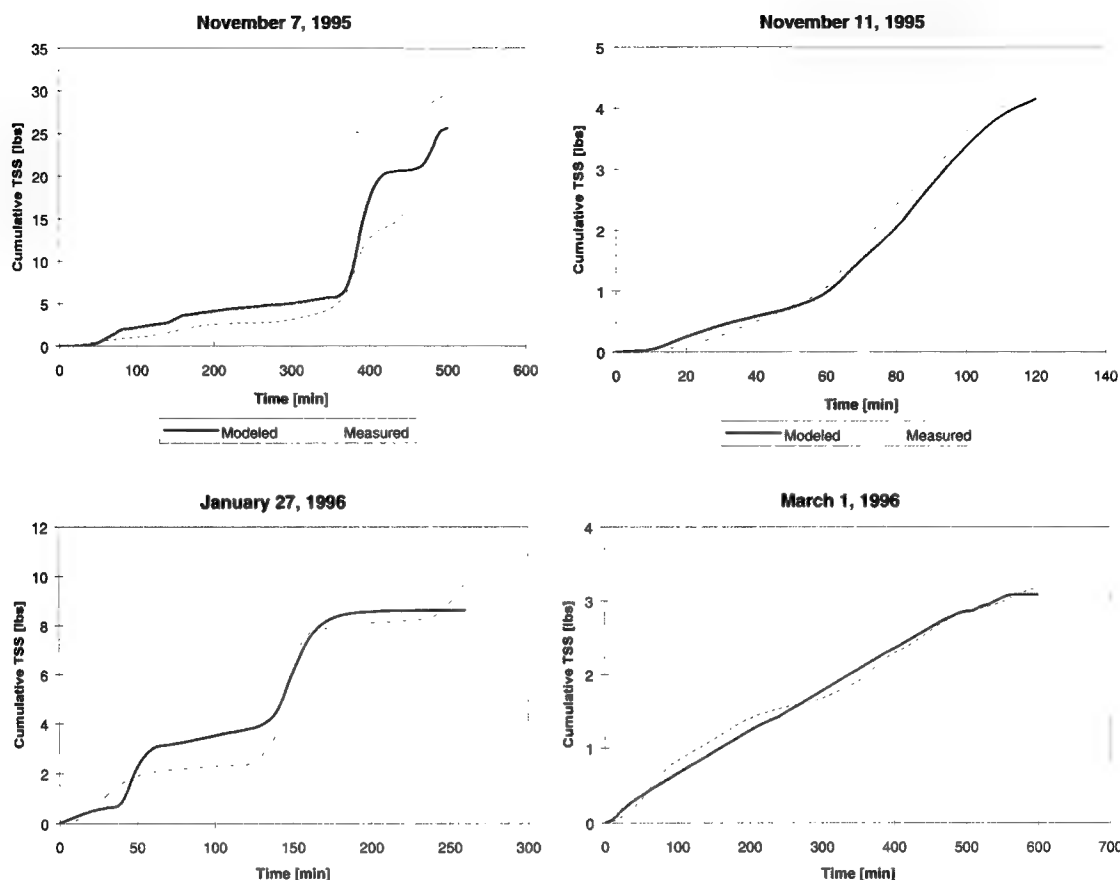
Figure 6. Modeled and Measured Cumulative TSS Washoff for the Indicated Storm Events.

SUMMARY AND CONCLUSIONS

A mathematical model has been developed for characterization of stormwater runoff from marine drydocks. The model has been tested for the quantity of runoff and for TSS loadings for several actual rainfall events monitored. The model results were found to be encouraging.

TSS is the only constituent considered in the mathematical model presented. However, a large number of rain-generated drydock runoff samples were collected and analyzed in the laboratory during the course of this study. Based on these analyses additional relationships are now being developed between the concentrations of total suspended solids and other constituents. These relationships will be published in the near future. With the addition of such relationships the usability of the mathematical model will increase significantly.

A major difficulty in the application of physically based models for drydock runoff is the description of the initial condition of the drydock surface prior to a storm. One needs to know

the initial amounts and distribution of pollutants over the drydock surface available for washoff. This information in a real life situation is very difficult to gather. Perhaps, empirical relationships can be developed to determine the surface conditions of a drydock as a function of the activities taking place prior to a storm. One needs to point out that this would be a rather difficult task because of the wide variations in the drydock activities. Also, monitoring the pollutant build up over a drydock surface without interfering with the drydock activities may become challenging.

ACKNOWLEDGEMENTS

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Characterization of Shipyard Wastewater Streams

Bhaskar Kura[1] and Raghuram Tadimalla[2]

ABSTRACT

More than 400 shipyards in the United States are involved in construction and repair of the ships and generate significant quantities of wastewater annually. Characterization of wastewater streams helps in segregation and subsequent handling of waste streams. This paper delineates various processes/operations in the shipyard that generate wastewater and gives the type of pollutants that may be present in those operations based on the method(s) employed. Surface preparation, metal plating and surface finishing, welding and metal cutting, machining and metal working, solvent cleaning and degreasing, and vessel cleaning operations constitute major sources for process wastewater from the shipyard. Wastewater analysis is required to know the strength of the pollutants in the wastewater stream. The pollutants present may be biochemical oxygen demand (BOD), total suspended solids (TSS), phenol, oil& grease, and some heavy metals. Once the constituents are known, segregation and employment of pollution prevention options such as source reduction, reuse and recycling, and treatment can be utilized to bring the strength of the wastewater stream below the discharge standards thus making it safe for aquatic life.

INTRODUCTION

The United States has over 400 shipyards involved in construction and repair of ships. Medium to large size shipyards generate as high as seven million gallons of wastewater annually. This quantity does not include sanitary wastes and stormwater. Such an enormous quantity calls for efficient management of wastewater in a way that meets the environmental standards, compliance and protection of the aquatic life. Efficient management of the shipyard

wastewater requires understanding of the pollutants present and their concentrations. Most of the management techniques like source reduction, waste minimization, control, treatment etc. can be effectively utilized once the composition of the waste stream is known. Therefore, characterization of wastewater is of prime importance. Characterization of wastewater not only helps in the understanding of the composition of the waste streams and the associated strengths but also helps in ways of implementing the pollution prevention options apart from reduction in costs.

Operations in the shipbuilding and repair industry are of large scale, and complex, and these activities generate significant amounts of multimedia emissions (solid, liquid, and air) but this paper focuses on wastewater emission sources. Major shipyard operations that generate wastes/pollutants include surface preparation, metal plating and surface finishing, solvent cleaning and degreasing, machining and metalworking, and vessel cleaning.

The characterization of wastewater is based on the process knowledge by looking into the raw materials going into the processes and also the product coming out from the process apart from analysis of the waste stream. The pollutants that come across in the shipbuilding industry have been described in the following sections depending on the processes. A brief explanation of the processes have been given for better understanding of the wastes that generate from them.

SURFACE PREPARATION[1,2,4,5,6,7]

State-of-the-art protective coatings, designed to give long term service life in adverse

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environments, require a substrate which is free of rust, mill scale, paint, and contaminants and has a surface profile to promote good adhesion. To achieve this condition, for both new steels and previously painted or corroded steels, it requires a mechanical or other erosion process to remove the contamination/surface layers and expose the bare steel substrate. Various methods are available to prepare metal surfaces for painting. The choice of the method to be used is based on several factors such as (1) whether the surface is painted or covered with rust scale, (2) which surface characteristics are required by the paint that is to be applied, (3) the size and shape of the surface to be prepared, and (4) the type of metal involved. Based on these factors, a suitable surface preparation method is employed. Some of the surface preparation techniques are given below owing to their potential to generate wastewater.

Wet Abrasive Blasting

Water has also been used in several forms for removing surface layers from steel. Water can be used by itself or in combination with abrasives or cleaning agents, and cleans by a combination of mechanical force and by dissolving or emulsifying contaminant materials. Wet abrasive blasting can be divided into two broad categories, air abrasive blasting with water addition, and water blasting with abrasive addition. One of the earliest methods developed was the water development process or water curtain method which projects a cone of water around the stream of air and abrasive as it leaves the nozzle. A simple water ring adaptor fits around the blasting hose nozzle is reported to reduce the airborne dust by about 50-75%. It has a minimal effect on the cleaning rate because the water does not mix with the abrasive. In the second type of wet abrasive blasting, the water is added to the abrasive just before it reaches the nozzle. Both these systems may use moderate pressures. Wet abrasive blasting can be used in most instances where dry abrasive blasting is used.

Hydroblasting

Evidence has shown that coatings applied on surfaces contaminated with soluble salts over a certain concentrations exhibit diminished performance. The new hydroblasting technique opens the possibility to clean coated and uncoated metal surfaces without the addition of solid abrasives. This technique virtually eliminates the problems of hidden local corrosion cells. The primary application of this technique will be for an older surface which has been rusted in saline environment rather than new steel. Instead of propelling a solid material as in abrasive blasting, hydroblasting entails the use of a cavitating high pressure water jet to remove rust scales and paints. These systems may use pressures as high as 50,000 psig[4] (ultra high pressure washing). Hydroblasting can be used in most instances where abrasive blasting is used. Further, it can be used to remove scales and deposits from heat exchangers and can also be used to remove rubber lining. However, this method is not as efficient and cost effective as the abrasive blasting[2,4]. The major problem associated with this type of blasting is flash rusting which can be solved by using inhibitors.

Chemical Stripping

Although grit blasting is probably the most effective method of removing marine growth and hull coatings, some surfaces, such as fiberglass, aluminum, or delicate steel parts, may require an alternative method[4]. Chemical strippers, such as methylene chloride-based solutions or caustic solutions, may be the most applicable. If properly ventilated, organic methylene chloride solutions give effective results in cleaning coated parts. Many times the surface preparation process begins with solvent cleaning to remove oil, grease, dirt, and other organic compounds. Inorganic compounds such as chlorides, sulfates, weld, flux, and mill scales are not removed by cleaning with organic solvents.

Small parts may be immersed in dip tanks containing a stripping solution. The parts must then be rinsed to remove the stripping agent. This process can often produce a large amount of contaminated rinse water. Some reduction in drag-out of the stripping agent can be reduced by allowing the parts to drain above the dip tank for a longer period of time.

Inorganic strippers, usually caustic soda solutions, can be used as a substitute to organic strippers in cleaning non-coated parts. It is very important that residues from alkaline solutions do not remain on the surface after cleansing. The major problems associated with inorganic strippers are the waste stripper being hazardous, and flash rusting of non-coated

parts. However, it is much easier to treat the waste on-site by neutralization and filtration before disposal into a sewer. The local regulatory authorities may require permit for this type of disposal. Table 1 lists surface preparation using chemical methods, materials used and pollutants expected in wastewater streams[3].

Wastes

The wastewater generated from the surface preparation process is from the above mentioned techniques. In case of wet blasting and hydroblasting, the wastewater consists of waste sludge with spent abrasive, paint chips, and surface contaminants. The wastewater from chemical stripping may consist of used organic solvents or caustic solutions depending on the type of stripper used apart from the surface contaminants.

METAL PLATING AND SURFACE FINISHING[2,3,4,5,6]

Metal plating and surface treatments are used in shipyards to alter the surface properties of the metal in order to increase corrosion or abrasion resistance, and/or improve electrical conductivity[4]. Metal plating operations can be categorized into electroplating and electroless plating processes. In electroplating, the metal surface acts as the cathode when electric current is passed through the solution containing metallic ions and forms an electrochemical cell. Ferrous and nonferrous objects are generally coated with aluminum, brass, bronze, cadmium, copper, iron, lead, nickel, zinc, gold, platinum, and silver.

Electroless plating uses similar steps as in electroplating, but involves the deposition of metal on a metallic or nonmetallic surface without the use of external electrical energy. Electropolishing is a similar process, different only in that the metal surface acts as an anode. Instead of deposition onto the surface of the object, a thin layer dissolves, leaving a bright, polished surface. Surface treatment includes, (1) chemical and electrochemical conversion, (2) case hardening, (3) metallic coating, and (4) chemical coatings[4]. Most surface treatment processes are completed in three basic steps, (1) surface cleaning and preparation, (2) modification, and (3) rinsing and finishing.

Chemical and Electrochemical Conversion

This process is designed to deposit a coating on the metal surface that assists in a corrosion protection, improves electrical conductivity, or prepares a surface for painting. The process includes, (1) phosphating, (2) chromating, (3) anodizing, (4) passivation, and (5) metal coloring of lettering. Phosphate coatings provide a base for the adhesion of paints and lacquers, and also provide protection against corrosion. Chromate baths often contain hexavalent chromium, sulphuric and/or nitric acid and other organic and inorganic activating compounds. These are usually used to minimize rust formation and to increase paint adhesion. Anodizing enhances corrosion resistance through electrochemical means. Passivation forms a protective film through immersion in an acid solution (nitric acid).

Case Hardening

Case hardening produces a hard surface that remains relatively soft, making the core soft and ductile and the covering hard and durable. Case hardening procedures include, (1) carburizing, (2) carbonnitriding, (3) nitriding, (4) microcasing, and (5) hardening using localized heating and quenching operations. Carburizing is the most widely used case hardening operation and involves the diffusion of carbon into steel surfaces at temperatures ranging from 845 to 955 degrees centigrade, resulting in a hard case in the high carbon area. Carbonitriding and cyaniding involve the diffusion of both carbon and nitrogen simultaneously into the steel surface. Nitriding involves the diffusion of nascent nitrogen into a steel surface producing case hardening. Additional description of case hardening methods can be found elsewhere[2,4]. Nitriding is accomplished using either in nitrogenous gas such as ammonia or a liquid salt bath.

Chemical Coating

This can be achieved through vapor deposition and vacuum coating. Chemical vapor deposition (CVD) is the gas phase coating method analogous to electroless plating, in that it is catalytic and involves a chemical reduction of species to a metallic material which forms the coating. These reactions require high temperatures ranging from 600 to 1500 degrees centigrade. In vacuum coating, the metal coating

is vaporized in a vacuum which is low enough to ensure that most of the evaporated atoms migrate to the work piece with a few collisions with background gas molecules. Ion vapor deposition (IVD) was developed from vacuum deposition in which aluminum is used as a substitute for cadmium plating on steel parts.

Wastes

Two important waste streams generated by surface treatment are spent alkaline cleaning solutions and spent acid cleaning solutions. These are generated by periodic replacement of contaminated solutions. Waste sludge is also generated in this process. Many wastes, some of which are toxic, are associated with waste streams emerging from electroplating operations. Major components of electroplating waste streams are the rinse water that is used to drag out the excess solution, and the spent cleaning and plating solutions. These may contain a variety of heavy metals and cyanides.

MACHINING AND METAL WORKING OPERATIONS[2,3,4,6]

The most common types of metal cutting processes are broaching, cutting, drilling, forging, grinding, milling, planing, polishing, reaming, sawing, shaping, stamping, threading, and turning. In most cases, the cutting tool travels along the surface of the work piece and shaves off the metal in front of it. The high friction at the cutting edge of the blade creates heat. If allowed to become excessive, this heat can permanently deform the part that is being formed, or the cutting tool. To prevent this undesirable effect, some form of coolant is needed. Usually, a liquid is supplied to the leading edge of the blade to create a medium with which the heat can be moved to a coolant sump.

Wastes

Wastewater expected from these operations may be classified as the hazardous waste and includes waste cutting oils and degreasing solvents. Metal chips are separated from coolants and recycled as scrap metal.

SOLVENT CLEANING AND DEGREASING OPERATIONS[2,4,6,7]

Shipyards use solvents in a variety of cleaning and degreasing operations including parts cleaning, process equipment cleaning, and surface preparation for coating applications. Some of the major solvents used are petroleum distillates, oxygenated solvents, and halogenated solvents. Most common cleaning and degreasing operations include cold cleaning and vapor degreasing[4].

Cold Cleaning Operations

Cold cleaning can be divided into four methods, (1) wipe cleaning, (2) soak cleaning, (3) ultrasonic cleaning, and (4) diphase cleaning.

Wipe Cleaning

Wipe cleaning consists of using a rag or towel that has been dipped or soaked in solvent to wipe a surface clean. Wipe cleaning is usually associated with maintenance operations or processes that fabricate parts on a single item basis, such as in the machine shop.

Soak Cleaning

Soak cleaning consists primarily of soaking parts in a tank of cold solvent or solvent solution. Heating units and agitators may be added to increase the efficiency.

Ultrasonic Cleaning

Ultrasonic cleaning relies on the use of high frequency sound waves to produce cavitation in a solvent cleaning solution. Cavitation results in the formation of small vacuum bubbles that immediately collapse after formation. The rapid implosion of these bubbles creates a cleaning and scrubbing action throughout the fluid.

Diphase Cleaning

Diphase cleaning combines a water rinse both before and after the solvent cleaning step into one operation. Halogenated solvents and water are relatively insoluble so that when placed together in a tank, they separate. The water will float to the top. This causes the parts being cleaned to pass through the water bath before reaching the solvent below. After removal, the parts are rinsed by the same water. In some systems, a small pump recirculates the solvent up into a spray unit. The excess spray and runoff from the part falls back into the tank and

sinks to the bottom. The part is then cleaned as mentioned before. These systems are usually fully enclosed to reduce waste due to air emissions.

Steam Gun Stripping

In this process, a mixture of non-halogenated solvents can be added to a storage tank and fed to the steam gun. A special valve controls the amount of solvent so that the surface can be sprayed with the steam and solvent mixture. Afterwards, it is rinsed with pure steam. This operation may require large quantities of steam, and it can also generate large amounts of contaminated rinse water.

Vapor Phase Cleaning

Vapor phase cleaning relies on 'hot solvent vapor' condensing directly on cold parts inserted into the vapor space of the degreaser. As solvent vapors condense on the dirty parts, the contaminants are dissolved. The dirty solvent falls to the bottom of the tank, is reheated and vaporized, leaving the contaminants behind. As opposed to a soak tank with used solvents, vapor phase systems maintain their cleaning efficiency because the parts are always exposed to clean solvent vapors.

Water-soluble Cutting Fluids

Water-soluble cutting fluids can often be used in place of oil-based fluids. The cutting oils usually consist of an oil-in-water emulsion used to reduce friction and dissipate heat. If these fluids need to be removed after the machining process is complete, solvents may be needed.

Aqueous Cleaners

Aqueous cleaners, such as alkali, citric, and caustic base are often useful substitutes for solvents. There are many formulations that are suited for a variety of cleaning requirements. Many aqueous cleaners have been found to be as effective as the halogenated solvents that are commonly employed. As aqueous cleaners do not emit fumes or vapors, large losses due to evaporation do not occur. Since most aqueous cleaners are biodegradable, disposal is not a problem once the organic or inorganic contaminants are removed.

Mechanical Cleaning Systems

In many cases, a high pressure steam gun or high pressure parts' washer can clean parts and surfaces quicker and to the same degree of cleanliness as that of the solvents they replace. Light detergents can be added to the water supply to improve cleaning. The waste produced by these systems is usually the oily wastewater.

Non-solvent Based Paint Stripping

Non-solvent based paint stripping methods are viable substitutes for solvent stripping. Paint stripping is normally performed by soaking, spraying, or brushing surfaces with a stripping agent such as methylene chloride, chromates, phenols, or strong acids. After the agent has remained on the part for a period of time, the surface is rinsed with water and the loosened paint is sprayed or brushed off. Aqueous stripping agents, such as caustic soda, are often employed in place of methylene chloride-based strippers. Cryogenic stripping utilizes the use of liquid nitrogen and non-abrasive plastic beads as blasting shot. Abrasive blasting is the most common form of non-solvent paint stripping in shipyards. The use of various metallic grit propelled at high pressure against the surface is very effective to remove marine coatings. Thermal stripping methods can be useful for objects that cannot be immersed. In this process, superheated air is directed against the surface of the object. The high temperatures cause some paints to flake off. The removal results from the drying effects of the air and the uneven expansion of the paint and substrate. Some paints will melt at high temperatures, allowing the paint to be scraped off.

Wastes

Major wastes and materials that become contaminated with the solvents in cleaning and degreasing are various types of solvents that are employed in the process. Liquid wastes include the aqueous cleaners used, liquids contaminated with solvents etc.

WELDING AND CUTTING OPERATIONS

The main structural frame-work of a ship is made out of various grades of mild and high strength steel. Though steel dominates in ships, aluminum and other materials are used for some

superstructures like the deck-houses of ships and other specific areas within the ship. Other materials include stainless steel, galvanized steel, and copper nickel alloy that are used for a variety of corrosion resistant reasons as well as structural integrity.

Various types of welding processes are used to join the different types of metals used in the construction of ships. Fusion welding, in particular, is performed at almost all locations in the shipyard. The choice of a particular type of welding process is made depending upon the customer specifications, production rates, and the operating constraints. For commercial shipbuilding, welding processes are subject to review and approval by the regulatory bodies of the United States Coast Guard (USCG) and/or the classification societies of the American Bureau of Shipping (ABS). An important factor in welding processes is shielding. At very high temperatures, a reaction with oxygen and nitrogen is rapid and has negative effects on the weld strength apart from rendering the weld impure. To protect against this, shielding from the atmosphere is required. In most welding processes, this shielding is accomplished by addition of a flux, a gas, or a combination of the two. Some of the welding and cutting processes are flux shielded metal arc welding (SMAW), submerged arc welding (SAW), gas metal arc welding (GMAW), gas tungsten arc welding (GTAW), flux cored arc welding (FCAW), plasma arc welding (PAW), gas welding, electroslag and electro gas welding, laser welding, electron beam welding, stud welding, thermal arc and gas cutting, and mechanical cutting.

Wastes

The waste generally depends on the methods and magnitude of welding employed. The waste generated by welding of thin metals by any method is the used diluted acids. The used acid waste is collected and managed as a hazardous waste. A considerable amount of slag and wastewater is produced by these processes except for GMAW where only wastewater is produced. The wastewater is sent for onsite/offsite treatment and other wastes such as slag are disposed as solid wastes.

VESSEL CLEANING OPERATIONS[2,4,6]

The term 'vessel cleaning' covers many different areas during the repair and construction of a ship or vessel. This work entails tank cleaning or bilge/ballast cleaning which in many cases generates a large quantity of waste which must be disposed of in an environmentally safe manner. The holding tanks that most yards use to store wastes from vessels being serviced may also be used as the repository for all the liquid waste generated at the yard.

A major portion of work at shipyards is repair work. Nearly all repair work requires vessel cleaning. The cleaning operation may be for maintenance cleaning, tank inspection, overhaul or major repair, cleaning for a change in cargo, cleaning after a contaminated cargo, cleaning in preparation for ballasting, cleaning prior to inactivation and activation of vessel, and engine room cleaning operation such as boiler line descaling and various degreasing operations. The various operations like tank washing, pipeline cleaning, mucking, chemical cleaning and chemical spot washing become a part of vessel cleaning operations.

Wastes

Wastes associated with vessel cleaning are typically generated outside the shipyard when the vessel is in use. However, because of the nature of the wastes and the way they are handled, the repair yard is frequently the generator on record. The most common of these wastes called bilge wastes is composed of wastewater containing oil and fuel removed from vessel bilges. Larger vessels may also generate sanitary wastes which usually can be discharged into a sewer directly, and chemical wastes which cannot be discharged into a sewer.

FIBERGLASS REINFORCED CONSTRUCTION OPERATIONS[2,4,6]

The manufacture of fiberglass ships and boats involve a number of process steps which are categorized as, (1) mold preparation, (2) resin preparation, (3) gelcoat application, and (4) fiberglass application[4].

Molds are used to give structure and support to the shape of the structure being built such as the hull of a ship or boat. Most molds are made of wood with a plastic finish. Most resins used in the process are prepromoted resins. Gelcoat

application involves application of a pigmented polyester resin or a polyester resin-based paint with a styrene content of approximately 30 percent. The application is with either an air atomizer or airless spray gun. This application is usually conducted in a spray booth. The catalyst can be added by hand mixing or by a plural component system which is injected through a separate line into the gun where it mixes with the resin. Once reheated, the polyester resin begins to thermoset. Once cured, the resin cannot be softened or reshaped by heat. The polyester resin lay-up operation results in the use of solvents. Acetone and methylene chloride are often used in this operation. These solvents are used to prevent clogging and to clean the operator's hands during clean up. For fiberglass application, the resin is either mixed, sprayed, or brushed onto the surface of the fiberglass material. The fiberglass material comes in a woven mat which is applied with the resin during fabrication.

Wastes

Wastewater generated from these operations consist of cleaning solvents from equipment cleaning and resin leftover in containers.

The above sections enumerate the different types of pollutants in wastewater streams resulting from the processes and/or operations in various shipyards. Sometimes, the wastewater streams include heavy metals as pollutants. Some processes generate liquid wastes which require handling as hazardous wastes. Such liquid wastes include wastes from photoshop, QAQC department, and other wastes like medical water, metal photo shop sealer, glue from carpentry shop, and solvents used for cleaning purposes. Great care has to be taken when heavy metals are present owing to their toxicity. Table 2 gives results of the analysis of pipe shop effluent. Though the concentrations may vary, Table 2 includes all the pollutants/parameters that may be encountered in shipyard operations.

There are other main streams of wastewater from the shipyard. They are sanitary wastewater and stormwater. The characteristics of sanitary wastewater are well known and need not be discussed in detail here. However, the stormwater characteristics may vary depending on the shops or operations located within the area of concern. The concentrations of pollutants from stormwater outfalls of a typical shipyard are given in Table 3.

The concentration of each of the pollutants of the wastewater stream is known by running analysis of the samples collected from the sources. In case of shipyards, regulations play an important role in managing the waste streams. Permits are required to discharge the wastewater generated in the shipyard. These permits generally specify the methods by which the pollutant concentration can be known. Irrespective of whether the state, local, or parish government is issuing the permit, the methods adopted are those approved by EPA (Environmental Protection Agency).

CONCLUSIONS

The characterization of wastewater streams generated in the shipyard is necessary owing to the significant quantities generated annually. Characterization helps in segregation of waste streams into hazardous and non-hazardous wastes and employment of pollution prevention options such as source reduction, reuse and recycling, and treatment.

Characterization of waste streams can be effected by knowledge of processes/operations in a shipyard that have the potential to generate wastewater. The wastewater generated from the surface preparation operations consist of spent abrasive, paint chips, and other surface contaminants. Wastewater from metal plating and surface finishing operations comprise of alkaline and acidic cleaning solutions. Similarly, wastewater streams generated by cleaning and degreasing operations contain aqueous cleaners and spent organic solvents. Other processes/operations in shipyards generate wastewater constituents of which are known by the method(s) employed in various operations.

It is advantageous to know the strength of the pollutants in the wastewater streams for better management of the same. This can be accomplished by analysis of the wastewater preferably by EPA approved methods. The pollutants present may be biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), phenol, oil & grease, and heavy metals. The type and strength of pollutants present in the wastewater

streams determines the type of treatment that can be efficiently applied to bring the wastewater below the discharge standards.

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Table 1. Selective shipyard processes, input materials and wastewater emissions

Process	Material Input	Wastewater Emissions
Metal cutting	Cutting oils, degreasing and cleaning solvents, acids, alkalis	waste oils (e.g., ethylene glycol) and acid (e.g., hydrochloric, sulfuric, nitric),alkaline, and solvent wastes
Solvent Degreasing and emulsion, alkaline, and acid cleaning	Solvents, emulsifying agents, alkalis, and acids	Solvent, alkaline, and acid wastes
Anodizing	Acids	Acid wastes
Chemical conversion coating	Metals and acids	Metal salts, acid, and alkaline wastes
Electroplating	Acid/alkaline solutions, heavy metal bearing solutions, and cyanide bearing solutions	Acid/alkaline, cyanide, and metal wastes
Plating	Metals (e.g., salts), complexing agents, and alkalis	Cyanide and metal wastes
Welding	Welding rods, flux coated wire, and other organic and inert gases	Diluted acids and wastewater
Painting	Solvents and paints	Solvent wastes
Other Metal Finishing Techniques (including Polishing, Hot Dip Coating, and Etching)	Metals and acids	Metal and acid wastes

Table 2. Wastewater characteristics of a typical pipe shop

Parameter	Concentration, mg/L
Biochemical oxygen demand	1358
Total suspended solids	660
Chemical oxygen demand	3720
Total organic carbon	1240
Cadmium	0.004
Chromium	0.015
Copper	6.3
Lead	0.187
Mercury	<0.002
Nickel	0.44
Silver	0.004
Tin	BQL; MQL = 0.020
Zinc	2.44
Oil and grease	133
Phenol	0.100

MQL = Minimum Quantification Level - USEPA Region VI NPDES; BQL = Below MQL

Table 3. Stormwater characteristics of a typical shipyard

PARAMETER	CONCENTRATION, mg/L			
	Outfall 1	Outfall 2	Outfall 3	Outfall 4
Oil & Grease (O&G)	3.0	7.0	2	1
Chemical Oxygen Demand (COD)	31.0	74.0	30	19
Total Organic Carbon (TOC)	8.4	14.3	7.7	7.3
Cadmium	0.02	0.04	0.06	0.09
Chromium (MQL= 0.10)	7.0	0.0	1	7
Copper (MQL= 0.10)	BQL	BQL	BQL	BQL
Lead (MQL= 0.005)	0.05	0.16	0.06	BQL
Tin (MQL= 0.02)	0.0	1.0	0	BQL
Zinc	0.02	0.04	0.02	BQL

MQL = Minimum Quantification Level - USEPA Region VI NPDES; BQL = Below MQL

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Regulation of Shipyard Discharges in Australia and the Potential of UV Oxidation for TBT Degradation in Washdown Waste Water

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ABSTRACT

The Royal Australian Navy uses tributyltin (TBT) antifouling paints on the major ships in its fleet. Tributyltin compounds are very effective antifoulants but have proven to be harmful to many marine organisms, and effects to non-target species have been observed in Australian inshore waters. Consequently, the use of these paints and release of tributyltin compounds into the environment have been regulated in many countries, including Australia. In Australia the regulation of TBT has been the responsibility of the individual states but it is now government policy to implement a total ban on antifouling paints containing TBT. The release of TBT contaminated wastes from shipyards and other vessel repair facilities is also coming under increasing regulatory control.

One major source of contamination is the water used to wash down ship hulls when vessels dock for repainting or refit. DSTO in collaboration with other commercial partners has been developing technologies to treat this TBT contaminated water. Contaminated wash down water has been demonstrated to be treatable using enhanced oxidation techniques. These processes produce hydroxyl radicals, which destroys tributyltin compounds by progressively converting them to much less toxic di-butyl tin, mono-butyl tin and eventually to inorganic tin compounds. Turbidity has been shown to significantly interfere with the process and trials are continuing to assess the level and type of pretreatment required.

INTRODUCTION

Tributyltin (TBT) compounds are broad spectrum biocides used in many antifouling paints to prevent the growth of marine fouling on ship hulls. These antifouling paint systems work by slowly and continually releasing a controlled amount of TBT which is toxic to most common fouling organisms. Once released into the environment, TBT readily partitions into sediments and the surface microlayer or is degraded in the water column with a half life of around 6 days. The half life of TBT in sediments is estimated to be 3.5 years (Batley, 1995). Consequently, TBT can be quite persistent in the marine environment.

TBT readily bioaccumulates and is extremely toxic to many non-target marine organisms. Important commercial species such as oysters and other bivalves have been adversely affected by TBT pollution. The NOEL (no observable effect level) of TBT for oyster larvae has been found to be as low as 20 ng/l, with considerable mortality occurring at 50 ng/l (Alzieu, 1991). In addition, the development of male characteristics on females, termed imposex, is thought to be induced in European mud whelks (marine snails) by TBT concentrations as low as 1 ng/l (Lewis, 1998). In Australia, shell abnormalities attributable to TBT have been observed in Pacific oysters in Tasmania and Sydney rock oysters in New South Wales (Batley & Scammell, 1991). Imposex has been detected in various

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gastropod species in Western Australia (Kohn & Almasi, 1993), South Australia (Nias *et al.*, 1993), Victoria (Foale, 1993) and New South Wales (Wilson *et al.*, 1993). In coastal waters near Perth, Western Australia, widespread contamination of TBT in the waters and sediments of the study area and the widespread occurrence of imposex in the gastropod mollusc *Thais orbita* were considered to indicate that TBT contamination of the coastal waters was an issue of extreme concern (DEP, 1996).

What exacerbates the problem, is that oyster beds and harvesting areas for many commercial species are often situated in bays, estuaries, and lagoons near harbours and marinas with high densities of pleasure craft and ships (Alzieu, 1991). High concentrations of TBT also occur near ship repair and drydock facilities (Lewis, 1993). Consequently, stringent limits for the use of TBT antifouling paints have been established which, in many Western countries, effectively prohibits the use of TBT antifouling paints on vessels less than 25 m in length (Batley, 1995). Regulations have also been imposed on land based operations to minimise TBT discharges into the marine environment. Further to this, at its meeting in November 1998, the Marine Environment Protection Committee (MEPC) of the International Maritime Organisation (IMO) resolved to implement a global ban on the application of paint containing TBT by 1 January 2003 and to a complete ban on the presence of TBT on ship hulls by 1 January 2008.

AUSTRALIAN POLICIES ON TBT

In Australia, regulation of the use of TBT antifouling paints has been the responsibility of the individual Australian States. The issues associated with the use of TBT in the Australian and New Zealand environment achieved prominence in early 1988 when detailed assessments of the use of antifoulants containing organotins were undertaken in New South Wales (Maltz, 1998) and New Zealand (Ministry for the Environment, 1988), and a conference was held to consider the Australian situation (Holmes, 1988). The issues were also addressed in New Zealand at around the same time. It was soon after this that Tasmania became the first Australian State to restrict the use of TBT, requiring all antifouling paints to be registered and imposing a ban on the use of antifouling paints

with a TBT release rate greater than 4 $\mu g/cm^2/day$. In early 1989, New South Wales introduced more stringent controls which banned the application of TBT antifouling paints to vessels less than 25 m in length. Other States followed suit using various statutory mechanisms.

As an example, in Victoria, the *Environment Protection (Organotin Antifouling Paint) Regulations 1989* were introduced under the *Environment Protection Act 1970*. These regulations stipulated that "a person must not use organotin antifouling paint on or apply it to or cause or permit it to be used on or applied to- (i) a ship which is 25 metres or less in length; or (ii) a pier, buoy, mooring or any other structure in marine or estuarine waters". Further, it stipulated that "a person must not use organotin antifouling paint or apply it to or cause or permit it be used on or applied to a ship that is more than 25 metres in length except with the prior written consent of the Authority." At the same time, proclamations were made under the *Agricultural Chemicals Act 1958* to prescribe tributyl tin to be prohibited for use as an agricultural chemical except where written consent was given by the Environment Protection Authority and to "declare the standard for tributyltin to be a maximum leaching rate into water of 5 micrograms per square centimetre per day of tributyltin from painted surfaces". These regulations sunsetted on 1 June 1999 and are proposed to be replaced by a *Notifiable Chemical Order for Organotin Antifouling Paint* (Bezzobs, 1999).

New South Wales, Victoria, Queensland, Western Australia and the Northern Territory all enacted controls limiting the use of TBT paints to vessels greater than 25 m in length and with release rates greater than 5 $\mu g/cm^2/day$. Tasmania and South Australia restricted the release rates only; no greater than 4 $\mu g/cm^2/day$ in Tasmania, and 5 $\mu g/cm^2/day$ in South Australia. The US EPA Method was accepted in all states as the method for determining TBT release rates (US EPA, 1996). The Royal Australian Navy (RAN) policy is generally to use TBT antifouling paints only on HMA Ships over 40 m in length (RAN, 1994).

Moves to achieve national consistency in the management of TBT were initiated in 1989 when the Environment Council, a forerunner of the present Australian and New Zealand Environment and

Conservation Council (ANZECC), set up an *ad hoc* working group to investigate the issues. Members of the Council include State and Federal Government Environment Ministers from both Australia and New Zealand. In 1992, as part of a broader examination of the environmental aspects of shipping, the Council established a Maritime Accidents and Pollution from Shipping Task Force. This prepared a strategy, after extensive consultation, that sought to coordinate actions on all possible impacts from shipping (ANZECC, 1996a, b, c). In regard to antifouling practices, the strategy included the following objective:

"Recognising that antifouling practices have improved in recent years, promote improved standards and best practice, and development and use of more environmentally benign antifouling practices by:
(i) adopting in general the IMO resolutions as the basis for Australian and New Zealand law, pending further review, to:
   (a) eliminate the use of antfouling paints containing organotins (normally tributyltin or TBT) compounds on non-aluminium vessels of less than 25 metres in length;
   (b) eliminate the use of anti-fouling paints containing TBT compounds that release more than 5 micrograms of organotin per square centimetre per day;
   (c) develop management guidelines for ship maintenance and construction facilities to prevent the release of TBT compounds into the marine environment from maintenance and construction facilities and run-off;
   (d) encourage the development and use of alternatives to TBT formulations that have minimal non-target effects;
   (e) conduct monitoring to evaluate effectiveness of adopted measures;
   (f) share information with interested parties;
(ii) supporting, as required, the review of the ambient standards for TBT in ANZECC's Australian Water Quality Guidelines (ANZECC, 1992);
(iii) monitoring and reporting on progress in introducing more environmentally friendly antifouling practices; and
(iv) reviewing overall progress every two years."

An outcome of this strategy was the completion of a consultancy which developed recommendations for:
(a) a draft code of practice for application, use removal and disposal of antifoulants and the fouling material
(b) a draft scheme for classification of marine protective coatings including antifoulants, and
(c) generic principles for assessing effects of antifoulants.

In late 1998 the Australian Government released the *Australia's Oceans Policy* (Anon. 1998a, b) with the position that the Government will:

- ban the use of tributyltin (TBT) antifouling paint by 2006 on vessels being repainted in Australian docks, unless the International Maritime Organization sets an earlier date for such a ban, in which case Australia will ensure it complies with any such arrangements noting Defence's operational requirements; and
- continue to promote the introduction of a global ban on TBT through the International Maritime Organisation.

AUSTRALIAN POLICIES ON DOCKYARD DISCHARGES

Australian States with controls over discharges have implemented these by requiring that shipyards and slipways are licensed, and imposing relevant conditions on the licence, Queensland was the first State to licence facilities to specifically address the issue of organotin wastes. The chemical control order specified that "a person could not use the chemical tributyltin other than at a place approved by the Minister". Approval of premises for the use of TBT based antifouling paints required:

- existence of a holding facility of a capacity to contain all water from the work area, including first flush stormwater;
- provision of suitable bund walls around areas where paint removal and application are to take

place to direct waste water to the holding facility;

- all first flush stormwater to be directed into the holding facility and to be prevented from entering the waterway
- provision of a lid over the holding facility to prevent excess rainwater from entering the pit during periods of major rainfall which may otherwise cause the pit to overflow, or alternatively an automatic facility to bypass the excess stormwater
- stormwater originating from outside the TBT work area to be diverted away from the work area
- work area to be totally above the limit of tidal influence
- techniques to be used which minimise aerial distribution of waste, ie low pressure water blasting and sponging (or wet slurry blasting) in preference to sand blasting; airless spray guns in preference to compressed air guns
- screens or enclosures to be used to minimise the aerial distribution of TBT

Other States are yet to enact similar controls, although New South Wales now requires that shipyards have a plan in place to contain, treat and/or dispose of contaminated wastes. In Victoria, the discharge of contaminated wastes is restricted under the general provisions of the Environment Protection Act which prohibits the discharge of any polluting material into waterways. In South Australia, the policy for licensing discharges specifies a maximum release rate of 5 µg tributyltin per $c\mu^2$ per day as a criteria for the protection of shellfish growing areas (EPCSA, 1992).

However, once contained, the wastes still have to be disposed of in an acceptable manner. TBT contaminated wastes are generally classified as prescribed wastes. This means that transport and disposal are subject to strict regulation. Depending on the waste, acceptable management options can include physico-chemical or biological treatment, incineration, immobilisation or, for solids and residues, landfill at approved sites. Liquid wastes can often be discharged to sewer after appropriate treatment, with the permission of the local sewerage authority.

A strong emphasis on reducing the amount of any prescribed waste at source is encouraged, and the economic expense of transport and offsite disposal of prescribed waste is further encouragement for such an approach. There is therefore a clear need for new treatment methods and processes to remediate TBT contaminated wastes.

As previously mentioned, one outcome of the ANZECC Maritime Accidents and Pollution from Shipping Task Force was the development of a draft code of practice for the application, maintenance, removal and disposal of antifouling paints. This code proposes that the application, maintenance and removal of all antifouling coatings should only be done at facilities capable of meeting New Zealand and Australian State, Territory and Commonwealth regulatory requirements for dangerous goods, occupational health and safety and environmental protection, and appropriate standards of best practice. Further, it proposes that Australia and New Zealand should work toward uniform licensing procedures for such facilities and that the sale of antifoulants should be restricted to these facilities.

For new facilities, the code proposes that "no water should run off work areas without treatment to remove toxic substances, turbidity and discolouration. New facilities should be designed and managed so as to allow for eventual disposal to sewer of treated waste water and first-flush runoff. The acceptable standards and quality of water for disposal into sewer would come under the jurisdiction of the local sewerage authority.

For existing drydocks, slipways and hardstands, the code proposes that "measures should be adopted to minimise water runoff and certain potentially toxic, turbid or discoloured discharges. Bunds may be used on sealed concrete, sumps to contain waste water and spillages, and strawbales and woven fibre material to retain suspended solids. Existing facilities should plan for upgrading to allow for eventual disposal to sewer of waste water and first-flush runoff.

The draft code of practice is still, as designated, a draft and is yet to be discussed in detail within ANZECC. Implementation is therefore still someway off. In the interim, control over discharges from ship and boat yards in Australia remains the responsibility of the States and subject to their will and initiative.

ENHANCED OXIDATION OF TBT CONTAMINATED SHIPYARD WASTE WATERS

During the operational life a ship, whenever it is drydocked, and prior to repainting, the underwater hull requires washing or hydroblasting to remove the biological slime and hydrolysed surface layer of the paint. This generates significant quantities of TBT contaminated waste water. TBT concentrations in washdown waters can exceed 5 mg/l, but are usually within the µg/l range. Where discharge has been permitted into adjacent waterways, discharge limits significantly below this have been set, for example 30 ng/l for one Australian facility. Disposal into sewer can also require a reduction in TBT concentrations and, if neither discharge is permissible, the cost for transport and disposal off-site can be high. Consequently, there is a need to find treatment methods that can reduce TBT concentrations to levels that are below the discharge limits.

Traditional biological treatment processes are not readily compatible with these wastes because of the extreme toxicity of TBT to many microorganisms. However, studies have shown that TBT compounds are susceptible to photodegradation. In a three-month study, Duhamel et al. (1987) showed that when tributyltin chloride and tributyltin oxide solutions were placed in sunlight, the TBT compounds were degraded, producing dibutyltin (DBT), monobutyltin (MBT), inorganic tin, and some polymeric organotins. Similarly, Komora and Popl (1978), using UV irradiation of tributyltin oxide found the same products after 24 hours illumination. Photodegradation, therefore, appears to be a promising technique to treat TBT contaminated wastewaters. Advanced oxidative techniques that produce hydroxyl radicals, a powerful oxidant, are methods whereby the rate of photodegradation may be enhanced.

DOCKYARD PROCESSES

In Australia there are three types of docks that are of a concern: dry docks, slipways and floating docks, and each will require different collection and holding facilities for both waste waters and abrasive blasting grits. It is anticipated that not all shipyards will be able to meet future requirements, and these dockyards will either close or restrict their operations to non-TBT painted hulls.

Washdown wastewaters from these dockyards vary enormously. The measured TBT concentrations have been found to range from 5 µg/l to 8 mg/l. The highest TBT concentration was recorded at a Victorian slipway, which was using a hydroblast pressure of 10,000 psi. In this case, large proportions of anti-fouling paint were being removed during hydroblasting. This is an extremely high value and includes both particulate and dissolved TBT. The washdown water from this slipway also contained dibutyltin (270µg/l) and monobutyltin (42 µg/l). This indicates that degradation of the TBT antifoulant is already occurring on painted and fouled surface.

It was also noted that at high hydroblasting pressures (in this case 10,000 psi) aerosol formation is also a significant environmental problem. This aerosol dispersion is difficult to trap and collect at present, and improvements here will depend on the design of improved hydroblasting equipment. However, a system designed to collect first flush stormwater will help contain some of this aerosol.

Dockyard washdown wastewaters are generally collected as run-off from the dock surface. During this, the waste will have ample opportunity to collect dockyard debris and other contaminants from the dock's other activities. It has been noted that oil and grease may also be significant components of stored washdown wastewater. Therefore, the final washdown wastewater that requires treatment will be quite a non-uniform and complex waste.

PRINCIPLES OF ENHANCED OXIDATION

Due to the toxic nature of TBT, a non-biological method was sought which could destroy TBT and minimise the contaminated wastes to go to landfill. Enhanced oxidation appears to meet these objectives. Enhanced oxidation is a term given to a number of technologies that produce hydroxyl radicals. Hydroxyl radicals are very powerful oxidants that can react quickly and vigorously with a wide number of chemical substrates.

Some of the more common enhanced oxidation techniques are listed below. Those with asterisks are the techniques DSTO assessed in the laboratory for treating TBT.

- Photocatalysis* uses visible light to excite a photocatalyst, the most common being the Anatase form of titanium dioxide. It has the advantage of using a cheap source of energy source (sunlight) but the reaction is limited to the surface, and reactor design is quite complex.

- Electrolytic oxidation uses similar semiconducting materials as the photocatalysis method, but the semiconductor material is excited electrochemically.

- UV/Oxidation* is another technique gaining favour. It uses 256 nm UV light to react with either ozone or hydrogen peroxide, which through various chain reactions produces the hydroxyl radical. The disadvantages are the higher cost of energy, but scaling up to a commercial unit is simpler.

- Fentons reagent uses a mixture of iron salts and oxidants.
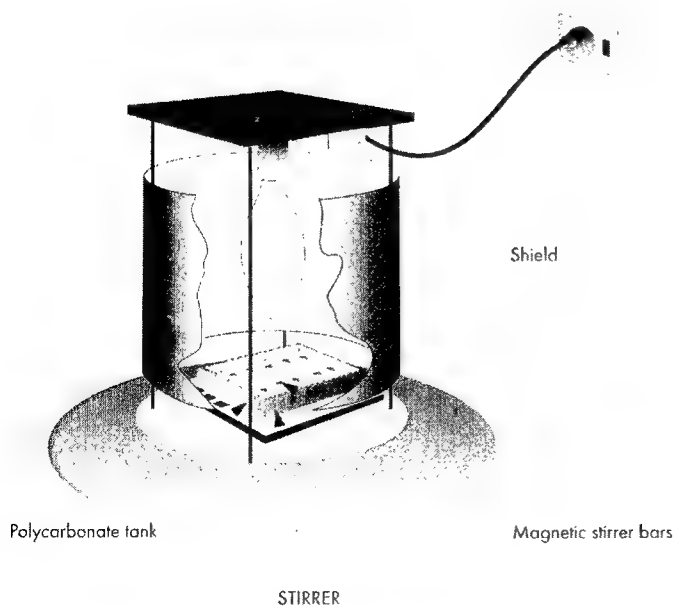
Figure 1. Schematic Diagram of the photochemical Test rig.

PHOTOCATALYTIC OXIDATION: METHOD

The photoreactor used for the experiments consisted of a 500 Watt mercury arc lamp which was suspended over a shallow polycarbonate tank measuring 300 x 150 x 70 mm (Figure 1). The tank and light were shielded with polished metal to reflect light into the centre of the photoreactor. The visible light intensity within the tank ranged from 340-720 $\mu Es^{-1}m^{-2}$, which is approximately a quarter of the intensity of sunlight. The contents of the tank were stirred with a multi-position magnetic stirrer.
Sampling was done at various time intervals with the lights off. The samples were promptly wrapped in foil and frozen until analysis.

Titanium dioxide in Anatase form was obtained from Kodak. Prior to use, the titanium dioxide was heated to 550 °C for 30 minutes following the method of Matthews (1983). Polycarbonate and teflon were the only materials in contact with the test solutions.

Organotins were analysed with a Varian Star 3400 gas chromatograph with flame photometric detector. TBT acetate was converted to TBT hydride by extracting 50 ml of sample with 5 ml of analytical grade hexane, 2 ml of a 4 % w/v sodium borohydride solution and spiked with a tripropyltin chloride internal standard (Tsuda *et al.*, 1986). The solution was shaken for 30 minutes. The separated hexane fraction was then concentrated by gently blowing nitrogen gas over the solution. During the extraction procedure the suspended titanium dioxide remained in the water phase and did not interfere with the separation. The detection limit was found to be 10 $\mu g/l$. Standard curves were obtained by adding varying amounts of a stock solution of tributyltin acetate, dibutyltin dichloride and monobutyltin trichloride in methanol, to 50 ml of deionised water and extracting using the same method as the samples.

PHOTOCATALYTIC OXIDATION: RESULTS

The result shown in Figure 2 is a typical example of the change in organotin concentrations with time, and the results obtained are consistent with a sequential dealkylation degradation pathway, where tributyl tin

is converted to dibutyl tin, then monobutyl tin, and eventually inorganic tin. Consequently, the hydroxyl radical is reacting at the tin-carbon bond and removing one butyl group each time. Importantly, the toxicity of the resultant product is reduced during each dealkylation stage. Therefore, complete mineralisation to inorganic tin will not be necessary to significantly reduce the toxicity of the effluents.
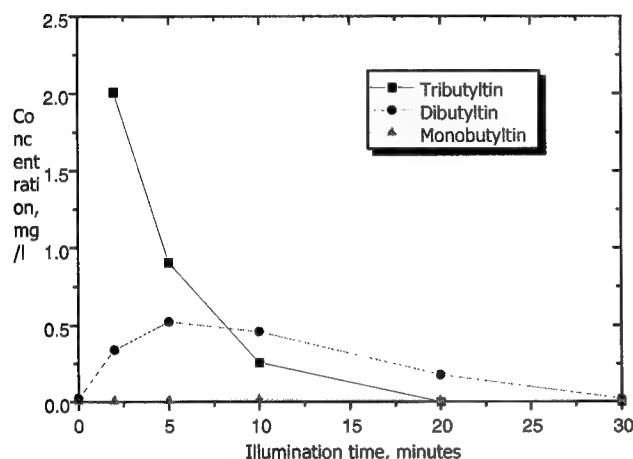
Figure 2 Typical Reaction Pathway

Another element of the observed reaction is that it is pseudo first order in character (Figure 3). Therefore, it is possible to calculate a reaction half-life for each experiment based on the slope of the line. This holds for all of the enhanced oxidation techniques so far tested with TBT. It also allows for easy comparisons, and for individual process optimisation.
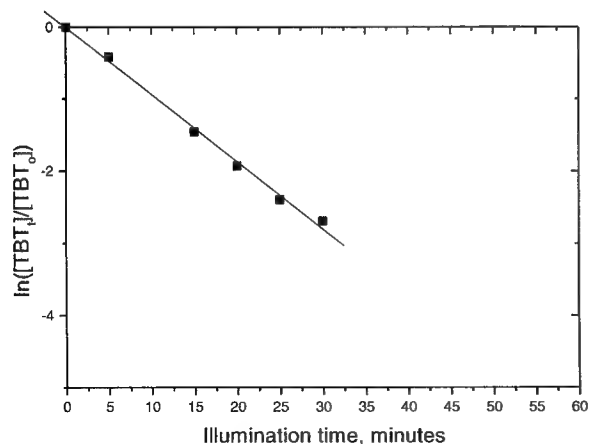
Figure 3 Pseudo first order reaction rate measured at pH = 9.3, titanium dioxide concentration of 1.0 g/l. The measured half-life in this instance is 7.4 minutes.

The photocalytic oxidation experiments produced results that were pH dependent. This is not surprising given that hydroxide can readily be converted to the hydroxyl radical by the photocatalyst. Table 1 summarises the results obtained using a model TBT waste water in the photocatalyst test rig.

These results demonstrate that the process does not provide a useful rate of reaction until the pH is around 12.6. This is going to be a major disadvantage for any meaningful process scale-up. Consequently, the decision was made to assess another enhanced oxidation technique.

Table 1. Photocatalysis of 2.5 mg/l tributyltin acetate in deionised water, using 2.0 g/l TiO_2, 380 nm UV light and pH adjusted using NaOH and HCl.

pH	Half life (minutes)
5.5	24.8
7.5	19.6
9.3	7.4
10.7	5.0
12.6	2.7

UV/OXIDATION: METHOD

UV/oxidation was assessed as having a number of advantages that made its investigation worthwhile. Firstly, unlike photocatalysis, the reaction is not confined to a surface and hence there is greater potential to maximise the amount of hydroxyl radical available to the process. In addition, because the reaction is not restricted to a surface, scale up to a commercial scale continuous process would be less technically challenging.

The UV/oxidation test-rig used in the following experiments was similar to the one for photocatalysis (Figure1), but a 256 nm UV light was used to illuminate the test mixture and the shape of the rig was altered to maximise light penetration. The test mixtures included pure TBT in deionised water, used for optimisation trials, and samples of collected dockyards washdown wastewaters. Hydrogen peroxide was added prior to illumination and again samples were taken at regular intervals and stored for later analysis. Initial blank experiments were performed using only UV light and only hydrogen peroxide. Neither of these experiments

produced a significant reaction rate with TBT. This confirms that the active process observed in subsequent experiments was hydroxyl radical formation and reaction with TBT.

Organotin concentrations in the text mixtures were determined using the same method as in the photocatalytic oxidation experiments.

UV/OXIDATION: RESULTS

Initial results showed that UV/Oxidation has the same reaction pathway as the one observed for photocatalytic oxidation (Figure 1). This was expected, as the underlying reaction is the same, hydroxyl radical oxidation of the tin-carbon bond. In addition the pseudo first order reaction kinetics were again observed.

To optimise the process, the effect of hydrogen peroxide concentration was assessed. Table 2 summarises the initial investigation of the UV/oxidation process using TBT acetate dissolved in deionised water with varying amounts of 42% hydrogen peroxide. The reaction half-lives observed for UV/oxidation are at least one order of magnitude faster than the results obtained using photocatalysis (Table 1).

The optimum rate of hydrogen peroxide dosing is around 0.3 ml/litre of standard 42% hydrogen peroxide. This would mean that 1 litre of hydrogen peroxide would be needed to treat each 3,000 litres of waste. The volume of waste washdown water produced varies with size of the ship and other factors but is often around 50,000 litres for a medium-sized ship and up to 2,000,000 litres for a large ship.

Table 2. UV/oxidation of 1.0 mg/l tributyltin acetate in deionised water and pH neutral.

H_2O_2 42%$^v/_v$ (ml/l)	Half life (minutes)
0.05	0.68
0.1	0.63
0.3	0.37
0.5	0.43
1.0	0.49
5.0	0.97

Therefore, about 40 litre of hydrogen peroxide would be needed for a medium ship, but up to 666 litres may be needed to treat the waste produced from a large ship. Therefore, for scale-up purposes an ozone generator may be more practical.

One of the common limiting factors with reactions involving light is the effect turbidity may have on the process, by shadowing the reaction. A series of experiments were performed with waste water collected from dockyards and slipways around Australia where ships hulls painted with TBT anti-fouling paints were being hydroblasted. Selections of these experiments are presented in Table 3. Some of these were given different pretreatments to remove solids.

Table 3. Half lives of various waste-water samples

Sample Number	Turbidity (NTU)	Calculated Reaction Half life (minutes)
1	53.1	10.5
2	1.7	7.3
3	2	4.1
4	2.2	2.5
5	NA	2.1

Results show that high turbidity does affect the degradation half-life substantially, but that reasonable reaction rates can be obtained for real dockyard washdown wastewaters, provided some pretreatment to remove suspended solids is performed.

Further work using collected dockyard waste waters showed that a few major variables can have a large impact on the composition of the waste water and subsequently can effect the efficiency of the process. A summary of the major variables are discussed below.

- Paint composition was found to have a large impact, and numerous TBT antifouling paints are on the market. However, one particular observation was the affect paint pigment was found to have. In particular, the black TBT anti-fouling paints used on submarines produced the slowest reaction rates. It is suspected that the lack of the titanium dioxide white pigment in the black paint may explain this.

- The extent of the fouling increases the level of soluble organic compounds in the waste, which may also be degraded by hydroxyl radical, and compete with the TBT.

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- As the pressure of the hydroblasting increases, more paint is removed, which results in higher strength wastes, putting more demands on the UV/oxidation process.
- How the waste is collected can also have a large impact, ie is it diluted with other wastes, is it allowed any settling, and does it pick up much additional debris.

FUTURE DIRECTIONS

DSTO is continuing to assess pretreatment options to develop a complete treatment option for dockyard wastes, and has established a partnership with Australian Water Technologies to develop and test a pilot plant based on the above scheme.

The cyclonic DAF is a new Australian invention for solids removal, which produces small air bubbles by cyclonic vortex. This reduces the need for high-pressure pumps that are required for more traditional dissolved air flotation devices. This unit will improve the economics of the process considerably, and is currently being assessed by Australian Water Technologies for the pretreatment process to remove suspended solids and turbidity.

A trial is being negotiated currently at a large Australian Dockyard.

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Real Time Copper Measurement
(Of US Navy Dry Dock Effluent)

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ABSTRACT

Due to its toxicity, copper is a high profile pollutant with many diverse sources such as ship hulls, process water and cooling water effluent. All fixed US Naval dry docks utilize a water collection system that allows process water (stormwater runoff, seawater leakage, freeze protection water, and ship discharges) to be discharged to the surrounding marine waters or to be diverted to a treatment system depending on the contaminant load. Current control systems typically monitor water flow into the system, and divert water for treatment under initial high flow conditions based on a premise that contaminant loads, particularly copper, increase when inputs, such as first-flush stormwater, are highest. A preferable method to monitor this process water would utilize a more relevant measure of contaminant load. While copper concentration would be one obvious parameter to measure, the ability to do so in a continuous, real-time manner, in an industrial setting, and at a reasonable cost has been problematic.

Key Words: Copper, Dry Dock, Effluents, measurement

INTRODUCTION

Currently, US Navy ships use copper-based paints for anitfouling. Aircraft carriers, the largest of these ships, contain over 1.3×10^5 m^2 of antifouling paint area. When ships are undergoing repair and maintenance in dry docks elevated copper levels in dry dock effluent is a constant concern.

In marine waters, copper can exist in various physico-chemical forms[1] i.e., dissolved, particulate, as a colloid, inorganically and/or organically complexed, or as a hydrated divalent ion. In the US, water quality criteria are set by regulators using dissolved copper concentrations. However, in National Pollution Discharge Elimination System (NPDES) permits copper discharges into marine waters are regulated using total copper concentrations. To further complicate matters, many researchers believe that the response of marine organisms exposed to copper toxicant correlates poorly with copper's dissolved concentration and is largely dependent on the hydrated divalent ion concentration ($Cu^{2+}_{(aq)}$). Until consensus is reached on what species of copper to measure, any real time automated copper instrumentation must have a tight correlation with total copper concentrations measured using standard laboratory techniques.

NEED FOR MONITORING

All fixed dry docks such as those found at US Naval Shipyards are required to collect and treat effluents exceeding permit levels. Flow rates at large dry docks may reach 4×10^8 L/day making treatment of all process water impractical and exceedingly expensive, with treatment cost typically around $(US)0.04/L. Fortunately, through best management practices the majority of water collected contains less than 10 µg/l Cu and does not require treatment.

The current flow rate diversion control systems are set to minimize discharge mistakes, which probably results in over treatment and unnecessarily high treatment costs. Based on once a week outfall monitoring, over a 4 year period at Puget Sound Naval Shipyard, a flow based treat or discharge system resulted in incorrectly discharging, rather than treating, approximately 4% of the time. This data does not indicate is how much process water is needlessly treated by this type of diversion control.

COPPER BASED CONTROL

To be a viable alternative to flow rate diversion control a copper based control system must be reasonably priced, able to operate in a continuous unattended mode, require minimal maintenance, be rugged enough to operate in an industrial environment, and the measurement must exhibit a tight correlation to total copper concentrations. This last criteria is the most difficult to meet for an online system. The major source of copper in dry dock effluent varies depending on the operations being conducted inside the dry dock. During docking evolutions, with a freshly painted hull the majority of copper is in the dissolved phase. While, during some ship maintenance tasks most of the copper will be found in metal alloy particulates.

INSTRUMENTATION

Recently two promising technologies have emerged that allow real time copper measurement. The first technology, the Trace Metals Analyzer (TMA), utilizes potentiometric stripping analysis (PSA), and is currently undergoing demonstration and validation under the Zero Discharge Industrial Waste Water Treatment Plant Project at the Puget Sound Naval Shipyard. The second technology utilizes a copper ion selective electrode (Cu-ISE) for measurement of copper activity in seawater. A system utilizing this sensor is currently being used to meet a NPDES permit requirement to monitor the copper levels of a power plant discharging 2.3G liters per day of cooling water effluent into the marine environment.

PSA

Potentiometric stripping analysis for metals was pioneered by D. Jagner[2]. This method monitors the voltage changes, at an electrode, during metal plating and stripping at the electrode. Through the use of standard additions the precise initial concentration of metals can be determined. An excellent summary of the technology can be found in the introductory text by J. Wang[3].

The TMA, utilizing PSA, preacidifies the effluent sample to below pH 2 before conducting an analysis. As can be seen from Figure 1 this enables the instrument to achieve, in marine waters, a close correlation with total copper laboratory measurements utilizing acid digestion and measurement with a graphite furnace atomic adsorption instrument.
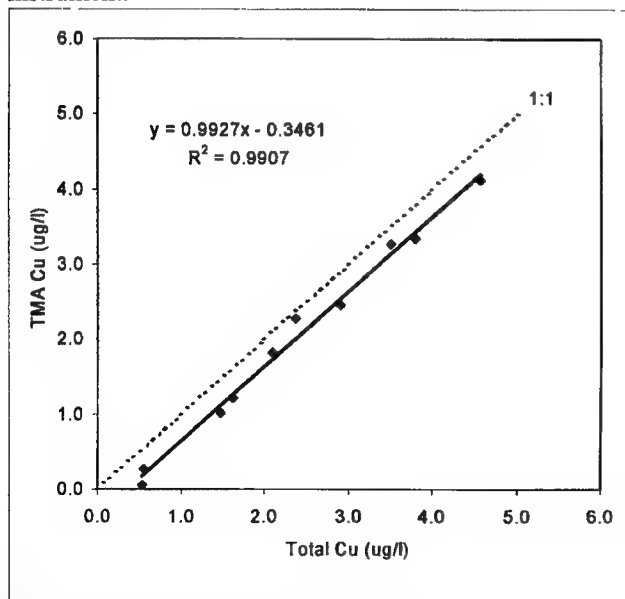
Figure 1. Copper levels from seawater samples collected from San Diego Bay. The copper concentration were determined using the Trace Metals Analyzer and graphite furnace atomic adsorption utilizing pre-acid digestion.

Although, the TMA is in excellent agreement with standard methods several factors make it less than ideal for dry dock monitoring. First, the TMA was developed as a laboratory/field instrument capable of generating data comparable to the best of laboratory methods. It achieves this accuracy in part by utilizing very high precision miniature pumps, which do not have the capability to survive in an industrial environment over long periods of time. Another drawback is cost. The commercialized cost will be around $(US)40k making wide spread use at a multi-dry dock shipyard facility expensive at best. Finally, the TMA is not a continuous flow through system. The sample rate, at maximum precision, is approximately four samples per hour. Sampling rates can be increased up to eight per hour at reduced precision.

Cu-ISE

The Cu-ISE system utilizing the Orion 94-29 electrode has been demonstrated to be an accurate tool for measurement of the activity of $Cu^{2+}_{(aq)}$ and in determination of marine water copper complexation capacity[4]. However, at natural marine water pH there is a poor correlation with total copper (Figure 2). DeMarco[5] shows that measurements made with the Orion electrode on marine waters acidified to pH 2 correlate well with dissolved copper measurements.

The advantages of the Cu-ISE are simplicity, ease of use, low cost, and a wide dynamic range (10^{-15} M - 10^{-1} M Cu^{2+}). In addition, industrial prototypes are currently in use measuring copper activity during in-water hull cleaning

Towards a Total Copper Instrument
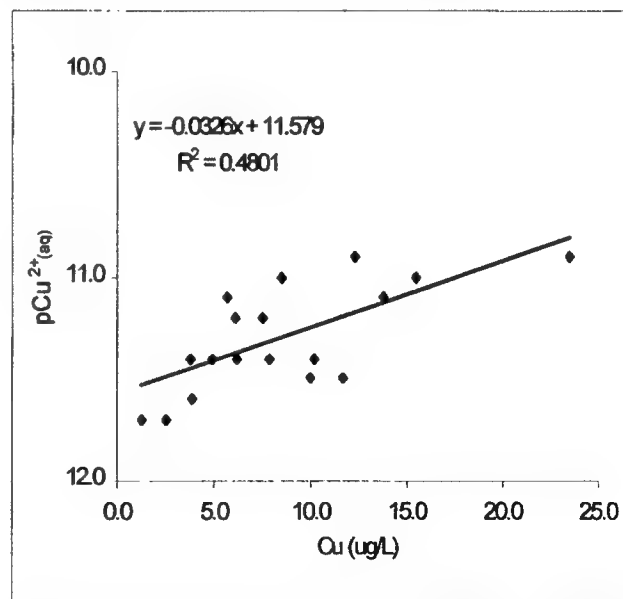
Figure 2. Correlation between total copper and copper activity, measured in pCu, at pH 8. The unit pCu is similar to pH in that it is the inverse log of the copper ion activity.

operations and monitoring the increase in copper activity of power plant cooling water discharges.

The difficulty in developing an instrument for measuring copper in dry dock effluents lies not in the sensing part of the equation, as discussed above, but in the in-line and real-time pretreatment of the effluent to release the tightly bound copper before it enters the
steel alloy particles. These fine particles are particularly resistant to extraction by low pH alone. Current work in this area is examining various approaches to this challenge. Ongoing development is examining the use of ultrasonics, ultraviolet radiation, pressure and heat, in addition to a lower pH.

The ideal inline system would utilize a Cu-ISE with a variable pretreatment system. This system would allow a sequential determination of the effluents copper speciation. This more complete picture would not only allow a treat or discharge determination, but would enable the dry dock operators to isolate problem sources of copper and assist them in determining the true impact of copper discharges on the environment.

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Discharge of Tributyltin
Into State of Virginia Waters

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ABSTRACT

The purpose of this paper is to review the impact of the Commonwealth of Virginia regulatory strategies, policies, and economic development projects related to the use of TBT in antifouling boat bottom paints. The Commonwealth of Virginia is the only State to have a NPDES Discharge Regulation for Tributyltin (TBT) at 50 parts per trillion as a discharge standard for discharged washdown wastewaters from shipyards and drydocks as means of reducing local environmental contamination from TBT.

The Commonwealth's concern about preventing the economic loss of business by Virginia shipyards to non-regulated countries and the impact on Virginia's shipping industry from increased fuel and operating costs led the Commonwealth of Virginia to establish a R&D Project at the Center for Applied Ship Repair and Maintenance (CASRM) in Norfolk, Virginia.

The purpose of this project (which is co-funded by the U.S. Environmental Protection Agency and the Norfolk shipyards) is to develop advanced technologies to remove TBT from ship washdown wastewaters.

Keywords: Commonwealth of Virginia, Tributyltin, regulations, NPDES, regulated discharges from shipyards, TBT advanced treatment technologies, washdown wastewaters.

INTRODUCTION

The first use of organotin as a biocide (toxin) in marine coatings and paints was to reduce biofouling (growth of plants and animals) on boat bottoms in the early 1970s. In 1974, oyster growers first reported the occurrence of abnormal shell growth in *Crassostrea gigas*, the pacific oyster along the East Coast of England (Key et al., 1976).

However, it wasn't until the mid 1980s, that researchers in France and the United Kingdom began to suggest that the use of TBT in antifouling paints was adversely impacting a number of marine species other than the fouling organisms. This economically important species is *Crassostrea gigas*, the pacific oyster, which is farmed in coastal waters of England and France (Alzieu, 1991; Davis et al., 1988; Thain, 1983; Thain et al., 1987; Waldock, 1986; His and Robert, 1983-1985; His, 1996 and references therein).

Subsequently imposex (development of penis) in female dogwelks was correlated to the presence of TBT in coastal waters (Davies and Bailey, 1991; Gibbs and Bryan, 1996; Gibbs et al., 1988, 1991; and Ten Hallers-Tjabbes et al., 1994).

However it was not until the mid 1980's that the effect of the use of TBT in antifouling paints was seen in the United States. Professor Edward D. Goldberg, of the Scripps Oceanographic Institute, has stated that "TBT is perhaps the most toxic substance ever deliberately introduced to the marine environment by mankind" (Goldberg,

1986). A deformed oyster was found in Coos Bay in Oregon by Wolniakowski et al. (1987).

Since the Pacific oyster is from Japan, in the UK, France, and the U.S., it is cultivated as a commercial species. It is the only species of oyster that has been found to demonstrate abnormal growth from exposure to TBT. The difficulty in delineating cause-and-effect relationships and the effects on untargeted species attracted national and international concern, see Champ and Seligman (1996); and de Mora (1996) for an overview of organotin environmental fate and effects.

Oysters in Virginia Waters

In Chesapeake Bay, Growth Abnormalities have not been found in the Virginia native species, the Eastern Oyster (*Crassostrea Virginica*), but larval toxicity is in the parts per billion (μg/L) levels. Oyster production in Virginia waters of Chesapeake Bay is a significant marine resource and economic base for local economies. Oyster production in the Bay has declined since the early 1980's. The difficulty in delineating cause-and-effect relationships and the levels measured in Bay and tributary waters attracted the interest of Virginia marine scientists.

After the implementation of national restrictions by the United States, France, United Kingdom, and others in the mid to late 80's, there has been about a decade of assessing the effectiveness of the initial regulations without subsequent additional or more restrictive regulations. Austria and Switzerland banned the use of TBT even though they are land locked. Japan banned the use of TBT in 1990. New Zealand's restriction of the use of TBT-based antifoulant paints in 1989 increased the use and marketing of copper-based marine coatings in the South Pacific as alternatives to TBT as being "environmentally friendly" (de Mora, 1996).

U.S. Regulatory Actions

In the U.S., regulatory actions for TBT stem from the Navy's Environmental Assessment of Interim Finding of Non Significant Impact (FONSI). The U.S. Navy reviewed the British studies by Thain (1983), Waldock and Miller (1983), Waldock et al. (1983), Alzieu and Portman (1984), and the French studies by Alzieu et al. (1981-1982); His and Robert, 1983-1985); and Alzieu et al. (1986).

The Navy's decision to not use TBT was based on: (1) excessive use of free-association TBT-based paints on small recreation boats in Europe, which were primarily used in shallow coastal estuarine waters where oysters were grown; (2) Navy ships were mostly seagoing vessels and spent only minimal periods of time in harbors or shallow coastal waters; (3) the Navy was proposing to use TBT-based co-polymer paints with low release rates, so that the impact on non target organisms would be very limited; and (4) the cost benefits from the use of these coating were estimated to be from $ 100 to $ 130 million annually in fuel avoidance (savings) costs and millions in annual maintenance costs (NAVSEA, 1984, 1986; Bailey, 1986; Eastin, 1987; Ricketts, 1987 and Schatzberg, 1987).

Subsequently, Virginia Senator Trible was concerned that the Navy would be able to use TBT and it would impact oysters in the lower Chesapeake Bay. He inserted language in the 1986 Report of the Continuing Resolution for the FY86's Federal Budget requiring to the effect that the Navy would have to have approval from EPA to use TBT. The Navy did not fully appreciate that the sensitivity of TBT in coastal states and by members of Congress and that EPA's regulatory process could prevent them from using TBT. The Navy's position was based on advice from its legislative advisors in Congress, that EPA would be able to easily give the Navy a variance for the

use of TBT, due to the reasons listed in the above paragraph. To the Navy's surprise, it subsequently learned that once EPA initiated the Special Review process that EPA would not be able to make any decisions until the process was completed.

The U.S. Environmental Protection Agency (EPA) on January 8, 1986, announced the initiation of a Special Review of all registered pesticide products containing TBT compounds used as biocides in antifouling paints and the Navy subsequently shifted to Copper-based antifouling paints.

About the same time, U.S., academic researchers and state water quality boards or state natural resource agencies in a few key coastal states (Virginia, North Carolina, California, Oregon, and Washington) began to closely follow the organotin issues in France and the UK, and investigated their coastal waters for similar effects. The only published paper finding deformed oysters in the U.S. is by Wolniakowski et al. (1997) for a specimen found in Coos Bay, Oregon. For additional information on TBT concentrations in U.S. and Canadian waters, see papers published in the Proceedings of the International Organotin Symposia (1986, 1987, 1988, 1989 and 1990). In addition, see the following citations and references cited therein: Seligman et al. (1996a and 1996b); Grovhoug et al. (1996); Maguire and Hale (1981); Maguire et al (1982; and 1986); and Maguire (1996).

The Antifouling Paint Control Act of 1988

Organotins are the only chemical compound regulated by law in the United States in which environmental legislation has been enacted solely for the chemical by name - The Organotin Antifouling Paint Control Act of 1988 (U.S. Congress, 1988). The purpose of the Act was "to protect the aquatic environment by reducing immediately the quantities of organotin entering the waters of the United States."

The prohibitions in the Act are: "No person in any State may apply to a vessel that is less than 25 meters in length an antifouling paint containing organotin" with the following exceptions: "(1) the aluminum hull of a vessel that is less that 25 meters in length; and (2) the outboard motor or lower drive unit of a vessel that is less than 25 meters in length."

No person in any State may: (1) sell or deliver to, or purchase or receive from, another person an antifouling paint containing organotin; or (2) apply to a vessel an antifouling paint containing organotin; unless the antifouling paint is certified by the Administrator [of EPA] as being a qualified antifouling paint containing organotin, and (3) sell or deliver to, or purchase or receive from, another person at retail any substance containing organotin for the purpose of adding such substance to paint to create an antifouling paint.

A key certification was that the EPA Administrator shall certify each antifouling paint containing organotin that the Administrator has determined has a release rate of not more than 4.0 micrograms per square centimeter per day.

In addition, the Act required the Administrator of the U.S. EPA, in consultation with the Under Secretary of Commerce for Oceans and Atmosphere (NOAA), was required to monitor the concentrations of organotin in the water column, sediments, and aquatic organisms of representative estuaries and near-coastal waters in the United States.

The Secretary of the Navy was to provide for periodic (not less than quarterly) monitoring of waters serving as the home port for any Navy vessel coated with an antifouling paint containing organotin compounds to determine the concentrations of organotins in the water column, sediments, and aquatic organisms of such waters. These monitoring programs were to remain in

effect for 10 years or until the last U.S. Navy ships coated with TBT paint had been removed from service.

Although OAPCA and subsequent U.S. EPA regulations allowed use of TBT coatings by large vessels, the U.S. Navy in 1989 decided not to use organotin coatings because of environmental concerns and the uncertain regulatory future at the State and regional levels. Following enactment of OAPCA, the following monitoring programs were conducted: (1) the in-house Navy monitoring studies from 1984 to 1987 in San Diego bay, Pearl Harbor, the Norfolk region and 12 other harbors, and Navy dry dock release rates studies that were conducted between 1989 and 1995, (2) the monitoring program that was required by EPA of the paint manufactures as part of the TBT permit process, and (3) the NOAA National Status and Trends Program added the analysis of TBT to their coastal monitoring program (sediment and oyster tissue) to establish a base line for commercially representative and important populations (Seligman et al., 1990; U.S. EPA, 1991; U.S. Navy, 1997).

COMMONWEALTH OF VIRGINIA (STATE OF VIRGINIA)

By mid 1987, most coastal states were planning or had implemented restrictions on the use of organotins. Virginia was among the first to become concerned and implemented a regulatory strategy developed by the Virginia Water Control Board after which the subsequent U.S. federal law was modeled. One of the areas that States could regulate organotin usage was linked to the ambient water quality concentrations of organotins through State Environmental Quality Standards.

Studies initiated in 1984 by Robert J. Huggett and others at the Virginia Institute of Marine Science for the lower Chesapeake Bay were finding high concentrations of TBT near drydocks and shipyards. See the following citations and references cited in Hall, 1986, 1988; and Hall et al., 1986, 1987; Huggett, 1986, 1987; Huggett et al., 1986, 1992, and 1996; Evens and Huggett 1991; and USEPA, 1987).

During 1986, a series of articles were written by Bruce Reid and published by the Daily Press/The Times-Herald, a local newspaper in Newport News, Virginia. Reid was the first in the U.S. to report on the impact of TBT on oysters in France and the U.K. and on the dangers and public health risks to shipyard workers applying TBT-based antifouling paints. He also reported on a variety of health problems that shipyard workers reported after they started welding and performing other work on the hulls of vessels painted with TBT. The workers symptoms included chronic skin inflammation, respiratory problems, headaches, stomachaches, burning eyes, dizziness, fatigues and frequent colds and flues. One article covered the lawsuit being considered by Charleston shipyard workers, due to a wide range of respiratory problems and constant headaches and coughing related to applying TBT-based paints. The possible human health risks to shipyard workers that were identified subsequently ranged from dermatitis to cancer. Shipyards in Virginia (that painted naval ships, cruise ships, and cargo vessels) supported the regulation of TBT because it would protect their workers.

Subsequently, after hearings in the U.S. Congress, key U.S. Congressmen from coastal states believing that the EPA regulatory process would be too slow, proposed the "Organotin Antifouling Paint Control Act of 1988" (OAPCA) which was signed into United States law by President Reagan on June 16, 1988. Coded in this law, P.L. 100-333, (33 USC 2401) are the United States Federal laws and regulations concerning the use (and subsequent disposal) of organotin compounds as additives or biocides in antifouling boat bottom paints. It should be noted that the concern for

TBT by leading U.S. researchers and the interest by the Commonwealth of Virginia helped Congress to quickly draft U.S. national legislation.

The predicted impacts of TBT regulations in the U.S. and the Commonwealth of Virginia by the chemical manufactures and paint companies (Gibbons, 1986) were:

- Higher fuel costs for shipping.
- Dramatic increase in operating costs for domestic vessels.
- Higher antifoulant protection costs to vessel owners.
- Deepsea vessels would go to foreign shipyards for painting.
- Severe hardship to u.s. shipyards (125,000 workers).
- TBT ban would push many shipyards over the edge, and foreign vessels, and shipyards would capture market.
- TBT painted hulls would still be in U.S. waters.

Virginia initially accepted the EPA advisory allowable level of 10 ng/L for salt water. However immediately upon passage of OAPCA, the Virginia Water Control Board indicated that it though that the level should be reduced to 1.0 ng/L (Commonwealth of Virginia, 1988) and was subsequently followed by the State of California with a level of 6.0 ng/L. Virginia also passed a state law that set the release rate at not greater than 4 μug/cm^2/day (U.S. Congress, 1987a; and 1987 b).

The Commonwealth of Virginia also was the only U.S. State to set National Pollution Discharge Elimination Standard (NPDES) Permit levels for TBT at 50 ng/L from shipyards and drydocks in state waters. It gave shipyards a 5-year compliance period that ended in September 1999 to meet this standard. Hull wash down is a 30 hour operation using 400,000 + Liters of wash water, resulting in TBT levels in wash down waste water ranging from 15,000 ng/L to 485,000 ng/L.

In 1998, it became apparent that shipyards were not able to comply with regulations using Best Management Practices (BMP's) and Best Available Technology (BAT). During this time period, it became apparent that Virginia shipyards could not effectively compete in the non-environmentally-regulated-global marketplace. Part of the problem was expertise to conduct R&D, and the cost of quickly developing a TBT waste treatment system that would achieve a regulated discharge (environmental water quality standard) level to protect local waters. The impact of not painting ships with TBT on the Hampton Roads economy has been estimated to be a loss of $ 340.2 million and 2,160 jobs (Godfrey, Jr., 1999, Personal Communication).

This led Virginia legislators at State and Federal levels to develop a cooperative R&D Project, which was initiated during the summer of 1999. The project is supported by the U.S. EPA, The Chesapeake Bay Foundation, and local shipyards in the Norfolk, Virginia area through CASRM (Center for Applied Ship Repair and Maintenance) at Old Dominion University to develop TBT wastewater treatment technologies for shipyards and drydocks to meet these standards. The need for this project stemmed from two CASRM projects funded by the NSRP on stormwater collection, characterization, treatment, recycling and reuse and discharge (CASRM, 1996, 1997).

SUMMARY AND CONCLUSIONS

The long-term economic and environmental public policy and regulatory strategies goals for antifouling marine coatings should be that vessels (regardless of length) need effective antifouling coating technologies and that this effectiveness not impact non-target organisms. The regulation of antifouling coatings is a genuine public policy concern because their selection influences the public costs for vessel shipped common goods, food, energy, etc.

Most effective antifouling coatings today contain toxic additive substances known as biocides. Organotin compounds have been found to be the most effective biocides developed to date. For a regulatory strategy to be supportive of the creation of high technology chemicals and products, it must include the promotion of continued research and development to push these compounds to additional refinements that enhance environmental attributes. This R&D must also include clean up and treatment technologies and systems, to be able to improve Virginia industries competitiveness in the global market place.

It is easy for regulation to have the unintended consequence of inhibiting economic development of products and technologies. The impact of regulations in Virginia has been a continued reduction in TBT levels in the marine environment since 1987 and control of point source discharges from shipyards now at less than 100 ng/L levels.

However, the Department of Environmental Quality of Virginia is still concerned about the lack of control on the largest non-point source of TBT to Virginia's coastal waters, since TBT leaching from vessel hulls in ports is not regulated and it believes that international regulation is required to reduce these levels.

The interests of the Commonwealth of Virginia are: reducing environmental and public health risks; protecting the marine environment; promoting economic development; competitiveness of Virginia shipyards, drydocks and ports (Virginia is home to the second-largest port facility on the East Coast), and creating jobs). The Commonwealth of Virginia has in place NPDES Discharge Permit Regulations to protect the marine environment and has funded R&D to develop TBT Waste Water Treatment Technologies for Shipyards and Drydocks. These actions will protect jobs in the seafood industry, shipyards industry and the shipping industry.

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Assessing the Degree of Appropriate Treatment of Shipyard and Drydock Wastewater Discharges and Stormwater Runoff

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ABSTRACT

Shipyards' and drydocks' (SYDD) wastewater discharges and stormwater runoff are currently being regulated to control the concentrations of chemical constituents in the discharges/runoff. The regulatory approach typically being used is based on worst-case assessments of the potential impacts of chemical constituents in the discharge/runoff as it may impact aquatic life in the receiving water column and sediments. This worst-case-based regulatory approach can readily lead to significant over-regulation, where SYDD are required to spend more funds in treating wastewater discharges and stormwater runoff than are necessary to protect the designated beneficial uses of the receiving waters for the discharges.

This paper presents an Evaluation Monitoring approach that will enable SYDD managers to work with regulatory agencies in assessing the appropriate degree of wastewater and stormwater treatment/management to protect designated beneficial uses of receiving waters without unnecessary expenditures. The focus of Evaluation Monitoring is on assessing the impacts of chemicals on aquatic life, and controlling these impacts in a technically valid, cost effective manner. This approach is significantly different from current regulatory approaches, which focus on chemical concentration control without regard to the aquatic chemistry/toxicology of the constituents of concern in wastewater discharges and stormwater runoff. Rather than measuring the concentrations of copper and then trying to extrapolate to aquatic life toxicity in the water column and sediments, Evaluation Monitoring focuses on using aquatic life toxicity tests to determine if the receiving waters for the wastewater discharge/ stormwater runoff are toxic. If toxicity is found, the constituents responsible are identified and, through forensic studies, their source is determined.

An area of increasing concern to boatyard and drydock managers is the use of co-occurrence-based sediment quality guidelines to "assess" the water quality significance of chemical constituents in sediments in the vicinity of their facilities' discharges. Based on co-occurrence-based "sediment quality guidelines," boatyard and drydock owners are being named as responsible parties for toxic hot spot contaminated sediment cleanup in "Superfund"-like actions. The co-occurrence-based sediment quality guidelines imply that there is a relationship between total concentrations of chemical constituents in sediments and some biological effect. However, it has been well-established for over 30 years that there is no relationship of this type, and that the total concentration of a constituent in aquatic sediments is an unreliable predictor of biological impacts.

The Evaluation Monitoring approach for assessing the water quality significance of chemical constituents in sediments focuses on determining whether there is toxicity in the sediments, and, if toxic, its cause and the source of the constituents responsible. This approach provides a far more reliable assessment of past and current wastewater discharges/stormwater runoff-associated constituent impacts on water quality than currently-used approaches.

INTRODUCTION

The development of a wastewater treatment system and stormwater runoff water quality management program from SYDD should involve a detailed evaluation of the characteristics of the receiving waters for the discharges/ runoff. The current approach for regulating wastewater discharges and the evolving approach for regulating stormwater runoff from SYDD is to require that the wastewaters/stormwater not cause or significantly contribute to exceedance of a water quality standard in the receiving waters for the discharge/runoff. Such an approach can result in large expenditures to construct and operate treatment works to achieve this level of constituent control, especially if it is applied to stormwater runoff associated constituents due to the large volumes that would have to be treated during major rainfall runoff events.

DEFINITIONS - TERMINOLOGY

One of the major problems within the water quality management field is a lack of common understanding of water quality related terminology relative to regulatory requirements and appropriate evaluation of water quality. This lack of understanding, especially as it relates to developing technically valid, cost effective water pollution control programs, leads to over-regulation of wastewater discharges and stormwater runoff associated constituents for which there are water quality criteria/standards. It also leads to under-regulation of real significant water quality use impairments for the unregulated constituents for which there are no water quality criteria/ standards. It is important to use such terms as pollutant, pollution, water quality, water chemistry, etc in accord with legal and technically correct usage to eliminate the inappropriate characterization of a water quality evaluation situation. The adoption of the following terminology would significantly improve the technical quality and cost effectiveness of managing water pollution.

Pollution. Pollution is defined in the Clean Water Act as an impairment of the beneficial use(s) of a waterbody. Finding chemical constituents in elevated concentrations in the water column or sediments is not pollution unless these constituents are impairing the beneficial uses of the waterbody.

Water Quality. Water Quality should be assessed based on the characteristics of the water relative to the beneficial uses of the water. Water Quality is not, as frequently used, a list of chemical constituent concentrations. In order to reliably assess whether the concentration of a constituent impairs the water quality - use impairment of a waterbody, it is necessary to evaluate on a site specific basis whether the constituent is present in toxic/available forms at a critical concentration for a sufficient duration to be significantly adverse to aquatic life that are important to the beneficial uses of the waterbody.

Water Quality Assessment. A water quality assessment is an evaluation of the beneficial use impairment that is occurring, or could potentially occur, due to the presence of a particular chemical(s) or other constituent. It is not an assessment of the frequency of exceedance of a water quality standard.

Water Quality Standard Compliance. Water Quality Standard Compliance is based on an assessment of the frequency of exceedance of a water quality standard in ambient waters receiving the discharge/runoff. Such compliance does not ensure that the beneficial use of the waterbody is being protected or that significant over-regulation is not occurring.

Administrative Exceedance. An Administrative Exceedance of a water quality standard occurs when concentrations of a constituent are present in waters above the standard without adverse impacts to aquatic life and other beneficial uses. For example, non-toxic forms of copper are present in a waterbody above a water quality standard that is based on copper toxicity.

Excessive Bioaccumulation. Excessive Bioaccumulation of chemicals occurs when the tissue residue-body burden within edible aquatic organisms exceeds US EPA or FDA regulatory guidelines. It is not an elevated concentration of a chemical constituent relative to background or so-called "NAS" guidelines. As whole organism tissue residue guidelines are developed to protect higher trophic level fish/shellfish-eating birds and animals such guidelines may be used to evaluate excessive bioaccumulation.

Aquatic Life Adverse Impact. In order for a chemical constituent to be adverse to the beneficial uses of a waterbody, and therefore be a pollutant, it is necessary that the chemical constituent cause an altered number and/or types/characteristics of desirable forms of aquatic life.

Cause of Aquatic Life Adverse Impacts. The association of elevated concentrations of a constituent in water and/or sediments with aquatic life toxicity or altered organism assemblages is not a valid basis for assessing the cause of adverse impacts. Site specific studies involving assessing cause and effect must be used to determine if chemical constituents in water or sediments are responsible for aquatic life related adverse impacts.

Aquatic Chemistry. Aquatic Chemistry is the physical, chemical factors/reactions that control the distribution of chemical species that impact how a chemical affects water quality-beneficial uses. It includes the transport (advection and mixing) and transformations-reactions (kinetics and thermodynamics) that control the concentrations of chemical species in a waterbody.

Aquatic Chemistry is not a list of the concentrations of chemical constituents found in a water or sediment sample. Such a list is a chemical characteristic, not chemistry.

Toxic Hot Spot. A toxic hot spot should be defined as an area in which there is aquatic life toxicity that is significant to the beneficial uses of a waterbody. Further, a toxic hot spot is an area which serves as a significant source of a

bioaccumulatable chemical that is present in edible organisms at hazardous levels. A toxic hot spot should not be defined based on exceedance of a water quality standard or sediment quality guideline.

One of the designation criteria that is used in the California Water Resources Control Board's BPTCP Policy is the finding that the concentrations of constituents in a water or sediments exceed a water quality criterion/standard. With few exceptions, the water quality criteria/standards are based on worst-case assumptions. Using exceedance of a water quality criterion/standard as the basis for designating a toxic hot spot is obviously technically invalid and can lead to over-regulation.

MANAGING WASTEWATER DISCHARGES AND STORMWATER RUNOFF FROM SHIPYARDS AND DRYDOCKS

Presented below is a summary of the issues that should be considered in developing an appropriate water quality management program for wastewater discharges and/or stormwater runoff from shipyards and drydocks.

Potential Water Quality Problems

Shipyards and drydock facilities wastewaters and stormwater runoff may contain elevated concentrations of a variety of constituents that, under certain conditions, may be adverse to the beneficial uses of the receiving water for the discharge/runoff. Of particular concern are heavy metals, oil and grease, and potentially toxic organics. Many of the constituents of concern in discharges/runoff are in particulate forms and, therefore, tend to accumulate in the receiving water sediments to cause these sediments to contain elevated concentrations of potentially toxic chemical constituents. As a result, there may be need to control both dissolved and particulate forms of chemical constituents in SYDD wastewater discharges and stormwater runoff in order to protect the designated beneficial uses of the receiving waters for these discharges/runoff.

Increasing attention is being given to requiring additional treatment of wastewater discharges from industrial/commercial facilities such as SYDD beyond the normal treatment that is typically practiced. This additional treatment can represent a significant increase in cost for managing wastewater associated constituents compared to that normally being spent today to meet the traditional treatment/discharge requirements.

Potential for Over-regulation

Traditionally, wastewater discharges from SYDD are regulated in accord with NPDES permits, which establish maximum concentrations of chemical constituents which are potential pollutants based on worst-case assumptions about the impact of the constituents on the receiving waters' beneficial uses. Application of this worst-case approach to wastewater discharges typically leads to increased cost of treatment compared to that needed to protect the designated beneficial uses of the receiving waters for the wastewater discharge. For stormwater runoff from SYDD, the increase in cost can be substantial, where large amounts of funds can be spent in developing and operating treatment works for which there would be little improvement in the beneficial uses of the receiving waters for the stormwater runoff.

This paper provides guidance on an Evaluation Monitoring approach that can be used to determine, on a site specific basis, the degree of treatment of SYDD stormwater runoff that is needed to protect the designated beneficial uses of the receiving waters for this runoff. While the focus of this paper is on stormwater runoff from SYDD, the issues and approaches discussed are, in general, applicable to managing wastewater discharges from these types of facilities, with particular reference to the need for additional treatment beyond the conventional treatment that is normally required.

Evaluation of Existing Water Quality Impacts

The first step in the development of treatment works for providing additional, beyond normal, SYDD wastewater discharges and for stormwater runoff is to determine the impact of the existing discharges/runoff on the beneficial uses of the receiving waters. The mechanical comparison of the chemical concentration/characteristics of the wastewater/stormwater to worst-case-based water quality criteria/standards can lead to erroneous conclusions about adverse impacts of the constituents present in the wastewaters/stormwater above water quality standards. The US EPA (1987) Gold Book criteria, as well as the 1995 (US EPA 1996) updates of these criteria, are designed to be worst-case, which would be protective of aquatic life and other beneficial uses under essentially all conditions. There are few waterbodies where the application of worst-case-based water quality criteria as they are being implemented into discharge limits does not result in excessive treatment compared to that needed to protect beneficial uses.

Need to Incorporate Aquatic Chemistry. It is recognized that concentrations of constituents in the receiving waters

above worst-case-based water quality standards can readily occur in most waterbodies without significant adverse impacts on beneficial uses. There are situations, however, where an exceedance of a worst-case-based criterion/ standard represents a significant potential threat to the beneficial uses of a waterbody. A basic problem with using US EPA water quality criteria as discharge limits includes the failure to properly incorporate the aquatic chemistry of constituents into their implementation as state standards and NPDES discharge limits. It has been well known since the 1960s that many chemical constituents exist in a variety of chemical forms, only some of which are toxic/available. Further, ambient waters and their sediments contain a wide variety of constituents which detoxify/immobilize toxic/ available forms of potential pollutants such as heavy metals, organics, etc. In general, it is not possible to reliably extrapolate from a concentration of a chemical constituent measured using standard chemical analytical procedures to the concentration of toxic/available forms in the receiving water. There are a wide variety of physical, chemical and biological factors that influence this extrapolation which are rarely quantified.

While the US EPA (1995) finally took the necessary action to focus the regulation of some heavy metals in ambient waters based on dissolved forms, even dissolved forms of some heavy metals in many waters tend to over-regulate because the heavy metals interact with dissolved organic matter to form non-toxic/non-available complexes. Allen and Hansen (1996) have reviewed the importance of considering trace metal speciation in application of water quality criteria to state standards and discharge limits. The US EPA has not extended the regulations of heavy metals based on dissolved form to the many other constituents that occur in particulate or dissolved forms where the particulate forms are non-toxic and non-available. This leads to over-regulation to many organics that tend to sorb onto particulates in waterbodies.

Duration of Exposure. A key factor that is not properly incorporated into the application of US EPA water quality criteria and state standards based on these criteria is the duration of exposure that various types of organisms can experience without adverse impacts due to toxic/available forms of a constituent. The current regulatory approach involving no more than one exceedance by any amount every three years is well known to significantly over-regulate most chemical constituents in most waterbodies. It too is based on worst-case-based assumptions that are rarely experienced.

The approach that has been adopted by the US EPA of basing the water quality criteria/state standards on a one-hour average or a four-day average concentration in the water of concern is more of the conservative nature built into these criteria/standards. The one-hour and four-day average criteria for acute and chronic criteria respectively are contrived for ease of implementation of a criteria/standard. They are not based on finding that an exceedance of a water quality criterion for acute and chronic toxicity above the criterion value necessarily represents toxic or available conditions.

Inappropriate Independent Application Policy. Yet another factor that makes the approach used for implementing US EPA water quality criteria into discharge limits is the US EPA's policy of independent application of the chemically-based criteria/standards, where these numeric values must be met even if properly conducted aquatic life toxicity tests show that the constituents of concern are in non-toxic/non-available forms. These issues were discussed by Lee and Jones-Lee (1995a). It is recognized that the appropriate approach for implementing US EPA water quality criteria involves the use of the criteria as a screen for potential adverse impacts, where the responsible parties for the discharge work with the regulatory agencies and the public in determining whether the exceedance of the criterion in a waterbody represents a real significant use impairment of the waterbody. This approach has been discussed by Lee and Jones-Lee (1995b).

Need for Site Specific Evaluation. A site specific evaluation should be conducted to determine whether a particular discharge of stormwater runoff or the residuals in a wastewater derived from SYDD are significantly impairing the beneficial uses of the receiving waters for the discharge/runoff. An Evaluation Monitoring approach (discussed below) of the type developed by the authors (Lee and Jones-Lee 1996a, 1997a, Jones-Lee and Lee 1998a) provides a technically valid, cost-effective procedure for evaluating the degree of treatment of wastewater discharges and stormwater runoff needed to protect the beneficial uses of receiving waters.

The Evaluation Monitoring approach shifts the emphasis in water quality evaluation and management from a chemical concentration based approach to a chemical impact based approach. For example, rather than focusing on the concentration of a potentially toxic heavy metal or organic and then trying to extrapolate from the concentrations measured in a wastewater discharge/ stormwater runoff or ambient water, Evaluation Monitoring screens for potential toxicity in the discharge/runoff and receiving waters using a suite of toxicity tests that utilize sensitive test organisms. If a discharge/runoff and the associated receiving waters are non-toxic, then it is possible to rule out a large number of the chemical constituents which are regulated based on exceedance of worst-case-based water quality criteria and state standards.

Similarly, for constituents that tend to bioaccumulate to excessive levels in edible aquatic organisms, causing these organisms to be a threat to human health through their consumption, Evaluation Monitoring focuses on screening edible fish/shellfish to determine if excessive bioaccumulation is a real water quality problem in a waterbody. If the fish in a waterbody do not contain excessive concentrations of potentially bioaccumulatable chemicals, then it is possible to assess that the discharge of such chemicals in stormwater runoff or wastewaters does not lead to excessive bioaccumulation. If, however, excessive tissue residues are found then it is necessary to determine whether the discharge of these constituents from a SYDD is in a bioavailable form and remains in this form or converts to this form within the receiving waters for the discharge/runoff.

Similar kinds of screening approaches are used in the Evaluation Monitoring approach, where impacts of nutrients are screened based on excessive growths of algae or other aquatic plants in the receiving waters for nutrient discharges. Excessive fecal coliforms are screened through beach closures that are hydraulically connected to the discharge, etc. Lee and Jones-Lee (1997b) have provided a detailed discussion of the approaches that should be used in the implementation of the Evaluation Monitoring approach. Evaluation Monitoring is a far more technically valid, cost-effective approach for determining whether existing discharge/runoff associated constituents are significantly adversely impacting the beneficial uses of a waterbody.

SELECTING STORMWATER RUNOFF BMPS OR WASTEWATER TREATMENT APPROACHES BASED ON WATER QUALITY CONSIDERATIONS

While advanced wastewater treatment processes designed to remove specific constituents in order to achieve a desired concentration in the receiving waters are well established, the traditional hydraulic-based best management practices (stormwater runoff BMPs) design, which focuses on removal of some of the particulates in stormwater runoff, is not appropriate. As discussed by Jones-Lee and Lee (1998b), it is becoming increasingly recognized that particulate forms of heavy metals and other constituents in stormwater runoff are in non-toxic, non-available forms and therefore their removal in a conventional BMP will not necessarily improve receiving water quality-beneficial uses. The valid approach for selecting an appropriate BMP for controlling real significant water quality use impairment associated with stormwater runoff involves the following components. This same approach is applicable to

determining the degree of additional treatment needed of wastewater discharges.

Review Existing Water Quality Characteristic Data for the Stormwater Runoff/Wastewater Discharges and the Receiving Waters

• Determine if there is an exceedance of a receiving water water quality standard that is caused or contributed to by the stormwater runoff or wastewater discharged by SYDD.
• Determine if a real water quality use impairment (pollution) of the receiving water is occurring in the receiving waters for the stormwater runoff/wastewater discharge that is due to constituents in the stormwater runoff/wastewater discharge. The purpose of this effort is to determine if the stormwater runoff/wastewater discharge is causing or significantly contributing to real pollution of the receiving waters for the stormwater runoff. This will assess whether the exceedance of the water quality standard is an administrative exceedance relative to the highly protective nature of worst-case-based water quality criteria/standards when applied to many constituents in most waterbodies.

• If an inadequate database exists to determine if a violation of a water quality standard or a receiving water use impairment is occurring, then initiate a water quality monitoring/evaluation program designed to evaluate whether a real significant water quality use impairment is occurring in the stormwater runoff's receiving waters. Use the Evaluation Monitoring approach in evaluating whether a real significant water quality problem exists in the receiving waters for the runoff.

Addressing Administrative Exceedances of Water Quality Standards

• If a water quality standard violation occurs without a significant use impairment of the receiving waters, then petition the regulatory agencies for a variance from having to meet water quality standards in the runoff/wastewater receiving waters based on there being no use impairment occurring in the receiving waters due to the stormwater runoff associated constituents. This effort will enable stormwater runoff/ wastewater discharge water quality managers to reveal and appropriately address the over-regulation that arises from the US EPA's Independent Applicability Policy and the use of worst-case-based water quality criteria/standards.

This variance should include the opportunity to adjust the receiving water standards/stormwater discharge limits and/or the designated uses of the receiving waters to protect the designated beneficial uses of receiving waters for the

stormwater runoff without significant unnecessary expenditures for chemical constituent control. These adjustments should be based on appropriately conducted receiving water studies that focus on assessing chemical impacts, rather than the traditional approach of measuring chemical concentrations and loads. The US EPA (1994), in their Water Quality Standards Handbook provides guidance on how the worst-case-based water quality criteria can be adjusted for site specific conditions. It is important to understand, however, that the Agency's approach for developing site specific criteria/standards can still lead to over-regulation since it does not fully account for the aqueous environmental chemistry of constituents as they may impact the beneficial uses of a waterbody.

Determining the Cause of the Pollution and the Source of the Pollutant

• If a water quality use impairment is found in the receiving waters for the stormwater runoff/wastewater discharge, determine the specific causes of the use impairment and, through forensic studies, whether the toxic/available form of the specific constituent(s) responsible for the use impairment is derived from the stormwater runoff/ wastewater discharge of concern. Also determine the relative significance of the stormwater runoff/wastewater discharge versus other sources of the specific constituents responsible for the use impairment as a cause of the use impairment. The relative contribution information is needed to evaluate the potential improvement in the receiving water water quality as a result of implementation of the proposed BMPs/ advanced wastewater treatment.

Selection and Economic Evaluation of BMPs

• Select a BMP(s)/treatment processes to control the specific constituents responsible for the use impairment. The BMP/ treatment process selection should be based on the specific chemical species that cause a water quality use impairment in the receiving waters rather than the total concentrations of the constituent. For example, focus the BMP on removing those forms of dissolved copper that are significantly adverse to beneficial uses in the receiving waters for the runoff rather than on total copper, much of which is in the non-toxic form.

Evaluate Cost Effectiveness of a BMP(s) in Controlling Significant Pollution

• If the development and operation of the proposed stormwater runoff BMP/wastewater treatment process appears to be economically feasible, then estimate the potential improvement in the designated beneficial uses that will occur relative to the unregulated or under-regulated

sources of the same pollutant(s) responsible for the use impairment.

• If the potential improvements in the receiving water's designated beneficial uses is limited compared to projected costs to eliminate the use impairment, then the community leaders, regulatory agencies, environmental groups and public groups that are interested in appropriate use of funds should be consulted to evaluate if the expenditures for stormwater runoff/wastewater treatment chemical constituent control is the best use of the funds potentially available to meet societal needs.

Evaluate the Efficacy of the BMP/Treatment Processes

• Evaluate the efficacy of the stormwater runoff BMP/ wastewater treatment processes in controlling existing use impairments as well as preventing new use impairments. The traditional approach of measuring the removal of a chemical constituent(s) across a structural BMP such as a filter, detention basin, etc. as well as wastewater treatment works does not evaluate whether the BMP/treatment process causes an improvement in the receiving water's impaired uses. BMP/treatment process efficacy evaluations must be based on evaluating the improvements that the BMP/ treatment process causes or, for new developments, is expected to cause in the receiving water beneficial uses. This will require site specific studies of the impact of the development and operation of the BMP/treatment works on the receiving waters' beneficial uses for the treated discharge.

Detection of Future Stormwater Runoff Water Quality Problems

• Develop an ongoing monitoring/evaluation program to search for subtle and new water quality use impairments. An important component of a properly developed and implemented stormwater runoff water quality management program is the funding of a stakeholder consensus-based monitoring/evaluation program to detect subtle water quality problems that were not detected in the initial search for real significant water quality use impairments. This program should be designed to detect new water quality use impairments that arise from the use of new or expanded-use chemicals that become part of stormwater runoff or wastewater discharges. The search for undetected and new problems should be repeated every five years to coincide with the NPDES permit cycle.

Watershed-Based Approach

• The stormwater runoff BMP selection and wastewater treatment plant facilities upgrading should be formulated/

implemented on a watershed-based water quality management program in which the stakeholders for the management of the stormwater runoff/wastewater discharge water quality and the beneficial uses of the receiving waters and downstream waters for the stormwater runoff/wastewater discharge that could be impacted by the runoff, work together in a consensus-based approach to formulate, implement and evaluate the stormwater runoff water quality management program.

Managing Contaminated Sediment Quality Issues

The aquatic sediments near SYDD often contain elevated and sometimes greatly elevated concentrations of a variety of chemical constituents that are potential pollutants that have been derived, at least in part, from wastewater discharges/stormwater runoff from SYDD. Increasing regulatory attention is being given at the federal and state level to managing the water quality impacts of chemical constituents in aquatic sediments. This is leading to the development of an aquatic "Superfund" - aquafund-like programs in which responsible parties are being designated to pay for contaminated sediment remediation. Further, the NPDES wastewater and/or stormwater discharge permits for suspected sources of the constituents that are present in the sediments at elevated concentrations are being modified to reduce the input of the associated constituents. The California Water Resources Control Board (WRCB 1998) has recently adopted the Bay Protection and Toxic Hot Spot Cleanup Program Policy that implements a California aquatic sediment aquafund. Lee and Jones-Lee (1998b) have discussed the significant technical problems with the BPTCP toxic hot spot cleanup Policy. This Policy, as adopted, will lead to inappropriate designation of toxic hot spots and the naming of PRPs for their remediation.

As discussed by Lee and Jones-Lee (1998a), there are situations where the discharge of hazardous chemicals in wastewaters and stormwater runoff to waterbodies causes significant water quality use impairments associated with elevated concentrations of chemical constituents in aquatic sediments. There are also many situations where elevated concentrations of chemical constituents in aquatic sediments that are potential pollutants such as heavy metals do not cause an impairment of a waterbody's beneficial uses. Because of the great cost of "superfund" aquatic sediment remediation programs, it is important to properly evaluate whether an elevated concentration of a chemical constituent in aquatic sediments represents a real significant use impairment that would justify the remediation of the sediments to remove the constituents that are causing the elevated concentrations.

Reliable Evaluation of the Water Quality Significance of Chemical Constituents in Aquatic Sediments

There is considerable misinformation on how to reliably evaluate whether a chemical constituent or group of constituents present in an aquatic sediment are significantly impairing the beneficial uses of the waterbody in which the sediments are located. There are basically two approaches being advocated. One of these is a chemical concentration approach in which an elevated concentration of a chemical constituent that at some locations and under certain conditions is in a form that is adverse to the organism assemblages present within or on the sediments. The other is a biological effects based approach which focuses on measuring chemical impacts rather than chemical concentrations.

There are situations where constituents in sediments that are of concern because of their potential to bioaccumulate to excessive levels in higher trophic level edible organisms (fish and shellfish) serve as important sources of hazardous chemicals in fish that are used as food. There are also situations where the elevated concentrations of potentially toxic or bioaccumulatable chemicals in sediments are in non-toxic non-bioavailable forms. It is well established since the 1960's that there is no relationship between the concentrations of chemical constituents in sediments and their toxicity/availability for bioaccumulation. As discussed by Lee and Jones (1992), Lee and Jones-Lee (1993a) and Lee and Jones-Lee (1996b) the toxicity/ availability of chemical constituents in aquatic sediments is determined by the concentration of many of the bulk parameters of the sediments such as TOC, sulfides, carbonates, clays, iron and aluminum oxides, etc. that interact with the potential pollutants to cause them to be non-toxic.

Some regulatory agencies at the federal and state level such as the US EPA (Keating 1998), have adopted or are in the process of adopting sediment quality guidelines based on co-occurrence based approaches, it is obvious that since this approach involves relating the total concentration of a chemical constituent in sediments to a water quality impact, that co-occurrence based guidelines are technically invalid. Lee and Jones-Lee (1993a,b,c, 1996b), as well as many others such as O'Connor (1999a,b) have discussed the unreliability of co-occurrence based guidelines. O'Connor (1999a) based on a critical review of the NOAA and US EPA data concluded, "*All these criteria are better than random selections in identifying toxic sediment but they are not reliable. They are all more often wrong than right and should not be used, by themselves, to imply anything*

about biological significance of chemical data." Co-occurrence of sediment based guidelines are unreliable and should not be used even as screening values to infer that a concentration of a chemical constituent in aquatic sediments is responsible for any water quality impacts that may be associated with those sediments. Such an association can readily lead to erroneous conclusions on the chemicals responsible for aquatic life toxicity and the sources of those constituents.

Suggested Approach. The approach that can be followed in evaluating whether elevated concentrations of a chemical constituent represents a potential cause of water quality impairment include the following.

Aquatic Life Toxicity
- Determine if the sediments are toxic using several sensitive test organisms and several appropriate toxicity test reference sites.

  Conduct toxicity tests at at least three sites in the area of concern quarterly for a year.

- If the sediments are toxic, determine if the aquatic life assemblages associated with the toxic sediments are significantly different from those present in the reference areas as well as nearby apparently less impacted sediments than those of primary concern.

  Determine if there is an aquatic organism assemblage gradient that is apparently related to toxicity in the sediments of concern.

- If there is a significant aquatic organism assemblage gradient that persists over a year that is apparently related to toxicity of the sediments of concern, evaluate the water quality significance of this toxicity.
  Also evaluate the potential improvement in the designated beneficial uses of the waterbody if the toxic sediments were remediated.

  It is important to note that this evaluation program has not thus far included any attempt to determine the cause of the sediment toxicity

- Reliably evaluate the potential cost of sediment remediation.

- If sediment toxicity appears to be a significant cause of a water quality use impairment and it appears to be economically feasible to remediate the contaminated sediments to eliminate the sediment toxicity, then proceed with evaluation of the cause of sediment toxicity.

Conduct sediment chemistry/toxicity investigations (sediment TIE's) to determine the constituents that are in the sediments that are responsible for the toxicity.
Do not use co-occurrence based sediment quality guidelines to "associate" the presence of chemical constituents in aquatic sediments that are toxic to aquatic life that cause significantly altered organism assemblages.

Excessive Bioaccumulation

- Determine if edible fish/shellfish from the waterbody preferably in the area of concern contain excessive concentrations of potentially hazardous chemicals that would cause the use of these fish as food to be a threat to human health. US EPA (1997) provides guidance on conducting bioaccumulation investigations.

  Use a human health based guideline consumption rate of one meal of local fish per week. Evaluate if this consumption rate is appropriate for local populations that are consuming the fish from the waterbody of concern.

- Determine the chemical characteristics of the sediments twice per year (late spring and fall).

  Determine the concentrations of the suite of heavy metals, PAH's, chlorinated hydrocarbon pesticides, PCB's and dioxins. Analyze the sediments for those chemical constituents that have been found to be present in excessive concentrations in edible fish taken from the waterbody.

  If the sediments of concern contain elevated concentrations of constituents that have accumulated in edible aquatic life tissue to cause the use of the aquatic life as food to be considered a threat to human health, utilize the US EPA/COE (1991, 1998) procedures to assess the bioavailability of the constituents of concern in the sediments. Also, measure the tissue concentrations of benthic invertebrates taken from the sediments of concern to determine if they have elevated concentrations of mercury for those situations where mercury has bioaccumulated to excessive levels in fish within the waterbody.

  This information should be used to determine whether the elevated concentrations of chemical constituents that are potentially bioaccumulatable in a sediment that are contributing to the excessive bioaccumulation problem within organisms taken from the waterbody in which the sediments are located.

Forensic Source Studies

In order to control the development of future contaminated sediments and, for that matter, water column toxicity/ bioaccumulation problems, it is necessary to reliably define the source(s) of the constituents that have been and/ or could be causing water quality problems. In some situations this is relatively obvious, in that there is a single discharger, such as a boat yard or a drydock, that is isolated from all other sources of the same types of constituents of concern responsible for the sediment or water column toxicity or excessive bioaccumulation. However, in many situations, such as in bays or in major urban industrial areas, there will be multiple discharges/sources of the same general types of constituents that are causing the water quality problem. Under these conditions it is necessary to conduct a reliable forensic study to determine the specific source(s) of the specific constituent(s) responsible for the adverse impact on water quality.

This type of study should not follow the approach recommended by the California Water Resources Control Board (WRCB 1998) in their Bay Protection and Toxic Cleanup Program (BPTCP) Toxic Hot Spot Policy of using elevated concentrations of constituents in the sediments to define the constituent(s) responsible for the toxic hot spot (toxicity source or source of the bioaccumulatable chemicals) in which a source of the elevated concentrations of the constituents is any discharger that has the same constituents in the discharge as were "associated" with the toxic hot spot. Such an approach is obviously technically invalid in that it ignores the aqueous environmental chemistry of chemical constituents that controls the toxic/ available forms of potential pollutants.

It is well understood by those with an elementary knowledge of aquatic chemistry/toxicology that all copper from all sources in all waterbodies is not equally toxic. The same situation applied to many other constituents. While tentative sources of potential pollutants can be identified through association based on elevated concentrations, detailed site specific investigations must be conducted to confirm that a potential source is in fact a real source of pollutants whose NPDES permit or waste discharge limits should be modified to control the input of pollutants.

These forensic studies must include detailed consideration of the aqueous environmental chemistry of the constituents of concern within the waterbodies of concern to determine whether a particular discharge of a potential pollutant of concern is toxic/bioavailable at the discharge and/or converts to toxic/bioavailable forms within the receiving waters for the discharge that accumulate/are

present at sufficient concentrations to cause a water quality use impairment at the point of concern.

When there are multiple sources of potentially significant constituents, then an attempt to quantify the relative contributions of each source should be made. Again, this should not be done based on a total concentration mass load approach. As discussed by Lee and Jones (1996d), it should be based on a site specific evaluation of the aqueous environmental chemistry/toxicology of the constituents derived from each source.

Funding of Site Specific Evaluation

While some potential dischargers of chemical constituents that could be adverse to the beneficial uses of a waterbody assert that it is the responsibility of the regulatory agency to prove that their discharge has or is, in fact, causing pollution-impairment of the beneficial uses of a waterbody, the burden of proof for water pollution control is on the discharger rather than the impacted public/regulatory agencies. However, in adopting this approach it is incumbent on the regulatory agencies to carefully specify the conditions under which potential polluters are designated. Approaches such as those adopted by the California Water Resources Control Board in its BPTCP Policy (WRCB 1998), in which "association" of elevated concentration of chemical constituents is used to designate a toxic hot spot, should be considered technically invalid since they can lead to frivolous designation of pollutants and/or responsible parties for contaminated sediment cleanup and NPDES permit modification.

It is important to understand that the adversarial regulatory system that exists today cannot tolerate frivolous designation of toxic hot spots. There are a number of examples where inappropriate designation of pollutants in sediments have been made using co-occurrence-based approaches that cause the public to have to spend large amounts of funds cleaning up contaminated sediments under conditions where this expenditure will not result in an improvement of the beneficial uses of a waterbody. This type of situation has been discussed by Lee and Jones-Lee (1993b).

The implementation of the incorporation of higher quality science and engineering into water quality management will require a substantial increase in site specific evaluations compared to the approach that is being used today to develop regulatory requirements for a particular discharge/runoff. In order to ensure that the funds needed to properly implement this more enlightened, technically valid approach are made available by the

discharger, the discharger should be given the option of either complying with worst-case-based chemical constituent control or complying with an appropriate assessment of the real impacts that chemical constituents in discharges/runoff have on the beneficial uses of a waterbody. Adoption of this approach would encourage dischargers, both public and private, to invest in appropriately conducted, watershed-based, stakeholder consensus developed receiving water evaluations in order to improve the cost effectiveness of expenditures for water pollution control.

A Technically Valid Water Quality Management Approach - A Water Quality Triad

There is growing recognition that the current water quality regulatory approach, in which a single exceedance by any amount of a constituent for which there is a water quality standard more than once every three years, is a technically invalid approach for cost-effective water pollution control. The US EPA, as part of adopting this chemical concentration based approach in the early 1980s, opted for a bureaucratic simple to administer but obviously, then and today, technically invalid approach.

While the Agency management staff claim that this approach is highly successful, in fact, as discussed herein, it is strongly contrary to the public's interests. In order to avoid massive waste of public and private funds chasing ghosts of problems associated with exceedance of a worst-case-based water quality criterion/standard, there is need to elevate the quality of science and engineering to the current level of understanding of how chemical constituents impact aquatic life and other beneficial uses of waterbodies.

The water quality triad approach is evolving as a regulatory approach in which the current science and engineering can be incorporated into defining a real significant water quality use impairment and the approach that should be used for its control/remediation. A water quality triad evaluation of potential beneficial use impairments of a waterbody is based on a non-numeric, best professional judgement, integrated assessment of information on aquatic organism assemblages, toxicity, bioaccumulation and chemical information. It involves determination of the numbers, types and characteristics of aquatic life present in a waterbody relative to the habitat characteristics. It also involves an assessment of aquatic life toxicity to a suite of sensitive test organisms relative to appropriate reference controls, as well as the use of chemical techniques (toxicity investigation evaluations) to determine, through toxicity assessments on the fractionated sample, the chemical constituents responsible for aquatic life toxicity.

The water quality triad should be implemented through a panel of experts in the topic area of concern, where this panel critically evaluates the adequacy of the current data/information base in defining a real significant water quality use impairment and the cause/source of the constituents responsible for the use impairment. If an inadequate database is available for a reliable evaluation, then the discharger(s) would work with the regulatory agencies and the public to develop the additional information needed. When this information is available it would be critically reviewed by the triad expert panel and a decision would be rendered by the panel on the magnitude of the water quality problem that exists, its significance to the public's interests and approaches with associated costs for its control/remediation. This information would then be used by the regulatory agency to implement a technically valid, cost-effective water quality management program.

Addressing Disagreements Among Experts

The current regulatory approach is largely based on an adversarial approach, where proponents (dischargers, regulatory agencies, environmental groups, etc.) of a particular position support their position without discussing the technical weakness of the position. If those in opposition to the position have adequate funding, they will hire consultants who will support their position. The regulatory board, which is typically composed primarily of lay members of the public, as well as the courts, are faced with trying to evaluate the technical merits of complex topics where there are what appears to them equal and opposite views/conclusions on issues. This situation frequently results in regulatory decisions being made which largely ignore current science and engineering that should be used to formulate public policy on a water quality management issue.

It is recommended that a public interactive peer review of technical issues be conducted in order to resolve disagreements among experts, including the water quality triad panel members, on complex technical issues. By adopting a public interactive peer review process anyone who peer reviews a topic must be prepared to defend these reviews in a public arena where those who find that the reviews are inadequate have the opportunity to point out the inadequacies of these reviews under a situation where the review board has the opportunity to hear an exchange of discussion of issues and receive written documentation with appropriate references in support of positions by the parties involved.

The peer review should not be conducted by a single individual but should involve the development of a peer review panel consisting of at least three knowledgeable individuals. The selection of the peer reviewers for the peer review panel should be a public process where the peer reviewers are knowledgeable and will take the time to fully review the pertinent information on the topic. They should review not only the regulatory board staff's discussion on issues, but also the comments made by others on the lack of validity of the staff's approach as well as those of the project proponents and others who commented on the issues.

The peer review panel should present the preliminary results of their reviews in a public meeting where the public has the opportunity to question and comment on the adequacy of the review. The reviewers then should be given the opportunity to make revisions in their review based on any new information obtained and develop a final review which is then submitted to the Board where again the public would have the opportunity to comment on its adequacy.

SUMMARY

The stormwater runoff BMP/improved wastewater treatment process development approach recommended herein is designed to transform the development of stormwater runoff BMPs from the current obviously technically invalid, non-cost effective traditional approach to one that incorporates mid-1990s science and engineering information into water quality management. Adoption of this approach will enable stormwater runoff water quality managers to select, implement and properly evaluate the efficacy of stormwater runoff water quality BMPs that will cost-effectively address real water quality use impairments in the receiving waters for the runoff in a technically valid manner. It will also enable those responsible for managing public funds to do so in a technically valid, cost-effective manner.

Additional Information

Additional information on these issues is available in the references listed below as well as in papers and reports developed by the authors that are available as downloadable files at the authors' web site, www.gfredlee.com. These publications contain references to the work of others that is pertinent to the topics discussed.

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Advanced Technologies for Removing TBT from Ship Washdown and Drydock Runoff Wastewaters

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ABSTRACT

Since July of 1999, with funding from the U.S. EPA, the State of Virginia, and a consortium of shipyards in the Norfolk, Virginia area, an extensive international search has been conducted to find or develop a treatment method or system to remove from TBT from ship hull washdown wastewaters that would normally be discharged to local water ways or to sewage treatment systems. The purpose of this research, development and demonstration project has been to achieve a reduction in wastewaters discharged from shipyards and drydocks that range from several thousand to several hundred thousand parts-per-million (ng/L) to less than 50 ng/L to protect marine resources in Chesapeake Bay.

<u>Keywords</u>:

Tributyltin (TBT), Discharges, NPDES Permit, Virginia DEQ, Shipyard Wastewaters, Advanced Waste Treatment, Carbon, DAF.

INTRODUCTION

TBT is highly toxic to some aquatic organisms at concentration levels measured in parts-per-trillion (ng/L). While it is used in a wide variety of industrial and commercial products, of most concern is its use in antifouling paints for ship hulls. Tributyltin was introduced as a biocide in antifouling paints over 30 years ago. It is said to be the most toxic material ever introduced deliberately by mankind into the marine environment.

In 1997, after 10 years of study, the United States Environmental Protection Agency proposed a national saltwater aquatic life criterion for TBT of 10 ng/L (62 CFR 42554, August 7, 1997). The Commonwealth of Virginia led the nation in developing a TBT standard, establishing in 1987, a surface water standard of just 1 ng/L and an NPDES discharge standard of 50 parts-per-trillion (ng/L). Virginia is the only state in the nation with a discharge standard for TBT. Some Virginia shipyards now operate under Consent Order deadlines, which mandate compliance with the 50 ng/L discharge limit by December 2001.

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The adoption of this standard has had a major impact on the Virginia ship repair industry. Shipyards generate TBT water from wash-down operations in dry-docks where fresh water is used to remove salt and slime from ship's hulls. This operation must be performed on all dry-docked ships. TBT levels in process waters from ship wash-down have been observed to be approximately 10,000 times higher than the new Virginia discharge standard. TBT is also generated from repair operations on sonar domes of US. Navy surface combat ships.

This paper describes efforts by the Virginia ship repair industry to achieve compliance with the 50 ng/L discharge limit.

BACKGROUND

Between 70 and 75% of the 27,000 deep water commercial ships have hulls coated with an antifouling paint containing TBT. These paints are used because they are extremely effective for preventing marine growth on the hulls, which can reduce ship speed and increase fuel costs. TBT is highly toxic to aquatic life at very low concentrations measured in parts-per-trillion (ng/L), see Champ and Seligman (1996).

The largest source of TBT in coastal US marine waters is that leached from the hulls of the thousands of ships which visit the US ports each year to load and unload cargo. This discharge is designated as non-point source and is unregulated in the United States.

A second and lesser source (but is a point source) of TBT from ships to the marine environment is when ships are dry-docked for standard hull inspection and certification (for insurance purposes) and or repair. The first operation in dry-dock is to wash down hoses the hull with high-pressure fresh water in order to remove marine salt and slime. This operation must be done to permit inspection of the hull and coatings, and in preparation for any hull repair work. A typical wash down job may generate over 100,000 gallons of wash wastewater, containing varying amounts of TBT from several thousand to several hundred thousand parts-per-trillion.

Virginia is the first state in the country to incorporate a numerical TBT limit for Virginia Pollution Discharge Control System (VPDES) shipyard permits. A consent order has been signed between the parties (DEQ, EPA and Shipyards) involved to meet a deadline of December 1, 2001 for Virginia shipyards for compliance with discharging water containing less than 50 ng/L of TBT. However, Newport News Shipbuilding has in its permit, compliance by June 4th, 2000.

Removing pollutants from industrial waste streams is fairly straightforward at levels of parts per million, It is much more difficult and expensive at levels of parts per billion. Purifying large quantities of water to levels of parts per trillion is a major technical challenge. At present, shipyards have no practical guidance on any technology that can be employed to meet regulatory discharge limits.

Over a period of 40 years, TBT has been the subject of many hundreds of studies that have documented the effects of TBT on different marine organisms(in different bodies of water). The effects of pH, water temperature, salinity and seasons of the year have been measured, as have the rate of decay of TBT in the environment, the fate of TBT in sediments, etc. Four international Symposia have been held related to fate and effects of TBT in the marine environment and a reference work has been published from some 40 years of studies (Champ and Seligman, 1996).

Notably missing from this body of knowledge is any work relating to the removal of TBT from industrial waste streams. There are a small number of papers relating to the fate of TBT in municipal wastewater plants using activated sludge (Fent 1996), but this involved low concentrations of TBT

(200 ng/L) in the influent water stream. Industrial waste streams from shipyards have measured TBT levels as high as 480,000 ng/L, which is known to be sufficient to kill the bacteria in activated sludge (Argaman *et al*, 1984). Additionally, water from dry-dock wash-down operations is intermittently generated, which rules out biological processes as a viable treatment option.

There is very little published information concerning the treatment of TBT in wastewater. Shipyards have no guidance on how to treat their water to remove TBT.

VIRGINIA SHIPYARDS' APPROACH TO ACHIEVING TBT COMPLIANCE

Virginia shipyards elected to work together cooperatively to address the TBT compliance challenge. Several years ago the shipyards helped establish the Center for Advanced Ship Repair and Maintenance (CASRM) as a cooperative partnership between the industry and the College of Engineering and Technology at Old Dominion University, Norfolk, VA. The CASRM consortium has since coordinated most of the shipyards TBT research, development and demonstration projects.

CASRM first commissioned a global bibliography of scientific papers (Alden et al., 1996) dealing with the adverse ecological effects of TBT. This bibliography detailed over 600 different scientific studies that defined the extent of the problem; however, there was virtually no information in the published work that could give guidance to shipyards on how to treat TBT in wash down wastewaters.

In 1997, CASRM began a project to determine the state-of-the-art technological practices regarding the reduction of TBT concentrations in wastewater (Messing et al, 1997). The National Shipbuilding Research Program (NSRP) funded this project. A survey was made of shipyards,

researchers, manufacturers of TBT, industries that incorporate TBT into their products, state and federal regulatory agencies, and Regional Water Control Boards, to gain information concerning TBT disposal in waste streams.

The purpose of this study was to identify practical technologies that could be used by shipyards to remove TBT from large volumes of water to levels below 50 ng/L. This study was based on: (1) a review of scientific and engineering literature, (2) a review of U.S. Patents, and (3) a survey of manufacturers and industrial users. The study concluded:

- **There is no "off-the-shelf" technology directly applicable to shipyard waste streams that will reduce TBT levels in water below a concentration of 50 parts per trillion.**

- **Because TBT is highly attracted to particles in water, adsorption process may prove be the most effective means to reduce TBT concentration. It is suggested that technology such as Dissolved Air Floatation, and Activated Carbon Adsorption are the best candidate technologies.**

Also in 1997, in the absence of any available technology, Norfolk Shipbuilding and Drydock Corporation (NORSHIPCO), a member of the CASRM consortium, decided to determine how much progress could be made toward meeting the <50 ng/L goal using different types of standard (off the shelf) water treatment equipment. Subsequently, NORSHIPCO assembled a small industrial water treatment processing plant to conduct some preliminary studies to treat the washdown wastewater using equipment leased on a trial basis. The equipment was not properly sized for the water flow, nor was it used in an optimum way. The results were, however, sufficiently

encouraging that water treatment was repeated on a series of subsequent TBT jobs, using variations of equipment to try different alternatives.

SUMMARY OF TREATMENT STUDIES AT NORSHIPCO, 1997 AND 1998

These studies were conducted on a large floating dry-dock having a smooth cambered deck on which heavy machinery could be easily relocated. With this kind of dry-dock, ballast tanks are flooded to sink the dock, the ship to be repaired is floated into the dock, and air is pumped into the tanks to raise the dock and the ship out of water. The average size of vessels included in this study was approximately 800' long and 100' wide, and having an underwater hull area in excess of 100,000 square feet.

Washdown is the first operation to be initiated as soon as the ship is out of the water. Typically this is done manually, using a crew of about 20 laborers, and continues through several shifts for a total of about 30 hours. Each operator uses a moderate pressure water washer, using fresh water only at a rate of 4 gpm. Typical water usage on this job is 140,000 gallons. The washdown serves to remove three materials from the hull: sea salt, a wet marine slime, which has the texture and appearance of dead algae, and the top layer of antifouling paint.

After washdown, the hulls of all the ships in this study were inspected, and in every case were found to be in excellent shape with little or no damage from corrosion or marine growth. This is testimony to the efficacy of modern TBT antifouling paints. Washwater was collected by ballasting the dock in order to tilt it slightly, so that all the washwater drains to one end, where it was collected in troughs on the apron of the deck. From here the water was pumped to holding tanks to await treatment.

Figure 1 provides a flow diagram for the experimental treatment system that has been developed following the NORSHIPCO experimental water treatment studies in 97 and 98. The equipment used in the NORSHIPCO studies included: (1) Dissolved Air Floatation to remove suspended solids, (2) a sand filter to remove fine suspended solids and (3) an activated carbon bed to remove dissolved organic materials including TBT. These technologies have been included in the design of the CASRM Barge Treatment System and Process Train, see Figure 1 below.

Water samples were sent to a commercial laboratory for analysis of TBT concentration and toxicity. TBT concentrations in different water samples collected from different treatment steps over time as ship washdown wastewaters were being treated is presented in Table 1 on the next page.
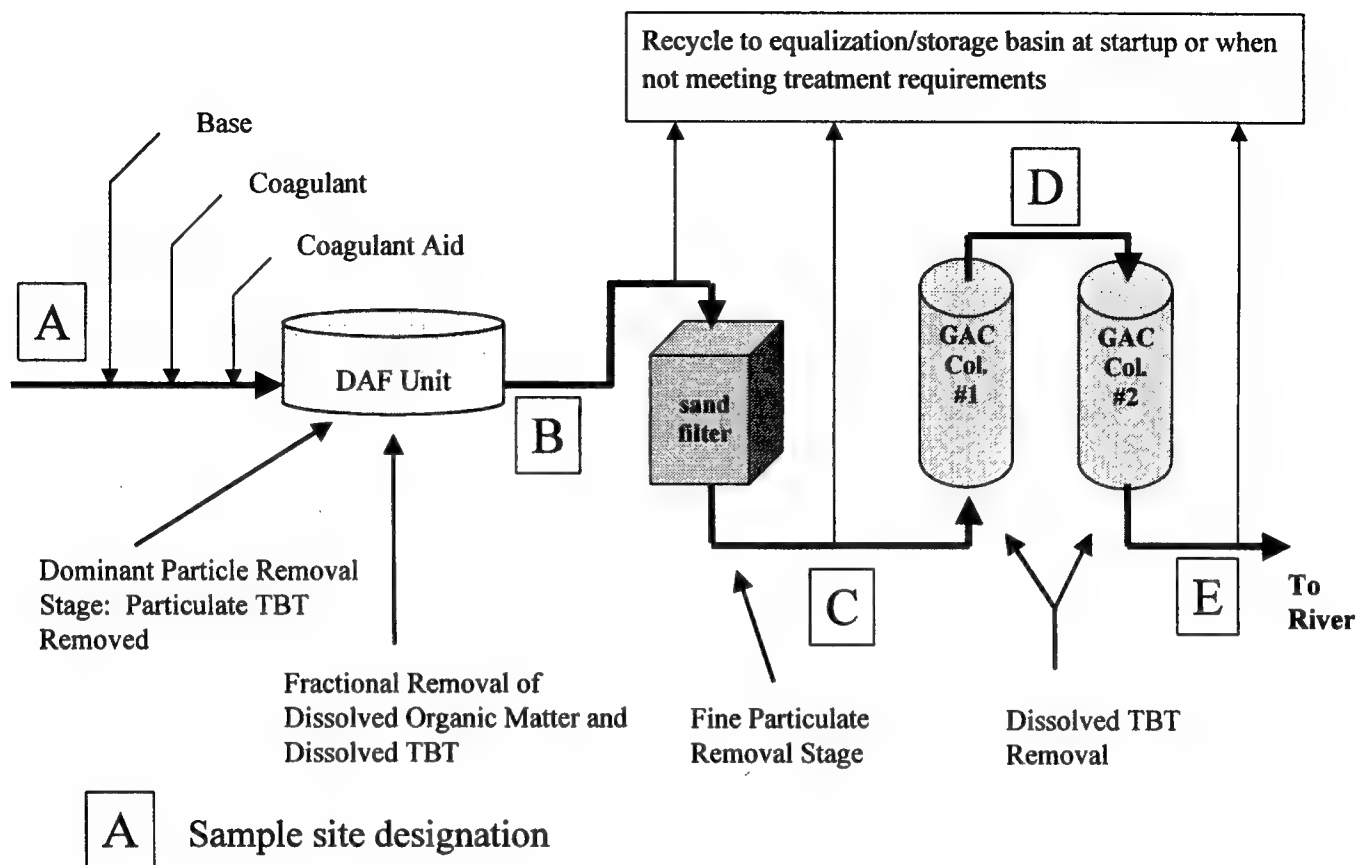
Figure 1. Schematic of the 1999 CASRM Barge Treatment Plant SYSTEM and Process Train for TBT Removal.

Table 1. Test results to remove TBT from shipyard wash water during 1997. Data courtesy of NORSHIPCO, Norfolk, VA.

Ship	Equipment Sequence	Treatment Stage	TBT Levels (ng/L)
Fascination 4/29-30/97	DAF; Carbon(1)	Pre Carbon	180,000
		Post Carbon	310
		Post Carbon	210
		Post Carbon	2,140
MV Po Hang Yu 7/2/97	DAF; Sand; Carbon (1)	Trough	8,300
		Pre DAF	11,000
		Pre Carbon	8,500
		Post Carbon	70
		Post Carbon	69
Zealand Expedition 8/2/97	DAF; Sand; Carbon (1)	Pre DAF	8,100
		Pre Carbon	8,000
		Post Carbon	790
Inspiration 9/12/97	DAF; Sand; see text	Pre DAF	485,000
		Post Carbon	18,000
		Post Carbon	41
		Post Carbon	210
Ecstasy 1/30/98	DAF; Sand; Carbon (1)	Post Carbon	540

The first set of data for the cruise ship Fascination found that the TBT concentration prior to passing through the carbon bed was 190,000 ng/L. TBT levels in wash water from all ships prior to passing through carbon absorbent varied from 8,300 ng/L to 480,000 ng/L. This may reflect different levels of TBT in different types of paint.

Activated carbon is very effective in removing dissolved TBT from water. The data from the Inspiration is particularly striking. The concentration of TBT in the water stream was reduced from 480,000 ng/L to 41 ng/L by passing it through the carbon bed. This level would meet the Virginia discharge limit goal of 50 ng/L. The key to effective TBT removal by carbon is effective removal of suspended solids by earlier stages, and providing for sufficient volume of carbon to handle the adsorption load.

It should be recognized that carbon would adsorb nearly all organic material presented to it, so it is important to reduce the presence of other organic contaminants in wastewaters as much as possible. Adsorption is a surface area phenomenon. As carbon adsorbs organic material, there is less surface area left and its adsorption efficiency drops as it becomes exhausted. Previous work by

CASRM on storm water runoff from a dry-docks suggests that non-TBT dissolved organic material may be several orders of magnitude higher than TBT concentration.

Over the five ship series, the TBT removal rate varied from 90% to 99.99%. On one occasion, the goal of <50 ng/L was achieved, but 12 hours later performance had dropped to 210 ng/L.

These tests at NORSHIPCO demonstrated the potential of a carbon based system to be able to remove TBT from wastewaters to below 50 ng/L, and focused attention on areas where further R&D was needed. A major concern was to refine and make the process more efficient and cost effective and to reduce the amount of carbon utilized and total waste residue.

The equipment utilized in the NORSHIPCO studies was not optimum; they were chosen because they were available off the shelf at the time. The DAF was rated at 25 GPM, but in order to keep up with shipyard production schedule, it was operated at rates up to 60 GPM. In addition the DAF was optimized for removal of metals (zinc and copper), not removal of TBT. The carbon bed was also severely undersized for the water throughput used.

Another difficulty experienced during these studies was the time delay between submitting water samples and receiving TBT analysis results. The commercial laboratory chosen routinely required three weeks to report TBT numbers. In many cases, the ship had left dry-dock before TBT levels in the water samples were known. Enquiries with various laboratories revealed that TBT analysis at levels of parts per trillion is very complicated, labor intensive, and expensive at these levels. In a laboratory set up to perform TBT analysis routinely, a minimum of two days is required per sample.

It became clear during these tests that a much faster (shorter time period) method for analyzing the water effluent was required. During the shipyard tests, the equipment was set up and operated during the wash-down without any real time knowledge of the TBT level in the effluent. A rapid method to assess TBT concentration is needed for treatment system process control.
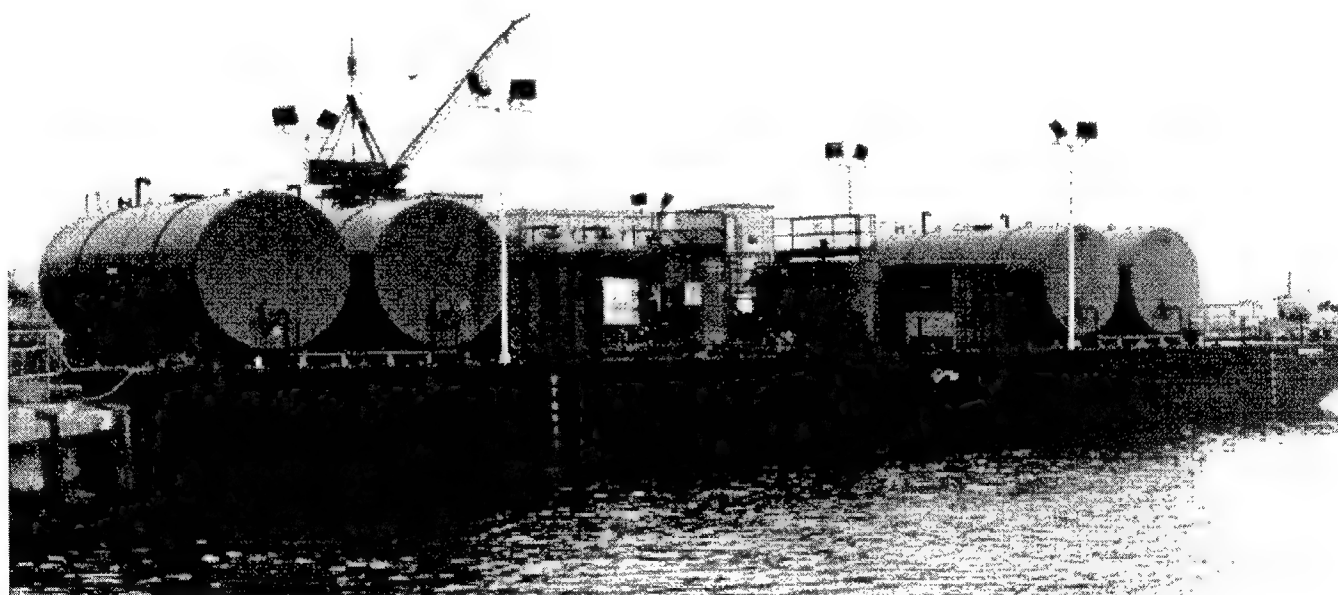
Figure 2. The CASRM Barge Treatment Plant SYSTEM and Process Train for TBT Removal.

CURRENT R&D

For the past year, the CASRM Consortium has been engaged in an intensive effort toward achieving shipyard compliance. Cooperative research and demonstration contracts from US EPA and the Virginia Department of Environmental Quality have enabled the CASRM Consortium to implement the following four-phase research and development implementation plan:

Phase 1. A full scale, fully engineered version of the 97/98 NORSHIPCO experimental system has been constructed, and deployed on a floating barge (November – December, 1999). The system, designed to treat 100 GPM, has a recycle type DAF system, a mixed media filter and two high-pressure carbon canisters. The carbon bed is sized to achieve a water-carbon contact time of over twenty-five minutes at full flow. The system is fully instrumented; operating variables are monitored and logged in real time by computer. There is provision to add other water treatment processes in the future. A photograph of the CASRM barge and water treatment system is presented in Figure 2. The System being barge mounted allows the treatment system to be moved conveniently to any dry-dock in the region where TBT washdown wastewater is being generated. The barge is completely self contained. It can be towed into place before the ship is dry docked, and can collect and process (treat) wastewater as soon as cleaning begins.

Phase 2. Laboratory analysis and bench scale tests will be used to optimize the barge based pilot plant treatment system and process and to evaluate alternative treatment processes, which may be utilized. Alternative processes include the use of oxidizers such as hydrogen peroxide and ozone, and the use of ultraviolet light to degrade TBT in wastewaters.

Phase 3. A FAST TBT Method for analysis of TBT in washdown and treated wastewaters is being developed. The current industry standard method of measuring TBT in water at concentrations measured in parts per trillion (ng/L) is complicated, labor intensive and requires a minimum of two days per sample to complete. A Fast Method for TBT analysis is required to monitor the performance of any treatment process developed to remove TBT. The goal is to be able to measure levels as low as 30 ng/l in less than ten minutes, which is the required QL level in the Consent Agreement.

Phase 4. The results of phase one, two and three will be combined and incorporated into development of a pilot plant water treatment system. This system will be tested under real industry production situations (100,000 gallon levels in 30 hours).

It is expected that this project will result in the development of a self-contained TBT treatment System to reliably achieve less than 50 ng/L TBT effluent. Design and operating data will be used to develop a design guide for modular TBT removal systems suitable for different conditions. The results will be disseminated to industry, the scientific community and the public. A Quality Assurance Project Plan (QAPP) has been prepared (Champ et al., 1999) to obtain the highest level of QA/QC for the entire project and full verification and validation of the FAST TBT Method.

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Process Water Treatment for the Removal of TBT in Ship Washdown Waste Waters

Peter L. Ashcroft[1] and David Abel[2].

ABSTRACT

A consortium is being created to commercialize a cost and environmentally beneficial water treatment process for the removal of TBT from ship washdown wastewaters developed in the UK at the University of Sunderland. The solvent extraction process, initially developed through funding from EC MEDSPA project, is to be exploited by a new group set up to introduce the technology to a wide range of industrial processes. A key target, for which the system was developed is treatment of TBT contaminated dockyard process effluent. The technology has been proven in one pass to reduce TBT levels from $2mg.l^{-1}$ to $200ng.l^{-1}$. The estimated cost for each metric tonne of effluent treated is £4 (<$7).

KEYWORDS: Tributyl-tin, wastewaters, ship washdown wastewaters, treatment, drydocks, shipyards.

INTRODUCTION

The development, testing and commercialization of this technology has been over a ten year period:

1991 University of Sunderland proposal
1992 EC MEDSPA support
1995 Pilot scale process demonstrated
1996 Joint-venture formed for scale-up
1997 $10te.hr^{-1}$ system proved

The extraction process is carried out by dispersion of an appropriate solvent in the process water stream. The dispersion provides an environment for mass transfer of the target species into the extraction phase (solvent). To achieve this end the solvent is dispersed to form a high surface area to enable mass transfer to take place. Once the extraction process is complete the solvent dispersion is coalesced for post-extraction treatment of the waste stream.

The development includes a patented process for development and maintenance of a large surface area at which interface the mass transfer takes place. The final part of the process involves the coalescence of the dispersed phase for separation and recovery / disposal of the target pollutant.

The new consortium expects to have a laboratory / pilot installation available early in 2000. This will be used to further evaluate performance and design the commercial units to be made available later in 2000.

OBJECTIVES & PROCESS OPERATION

The consortium objectives are to promote and exploit the technology because of what are seen as substantial process benefits. These are clearly apparent when the process is compared to alternative technologies applied to TBT and similar water treatment problems.

The benefits of this technology include:

a) minimization of waste volume;
b) no generation of solid waste;
c) avoidance of civil works;
d) design as a mobile, modular system;
e) parallel operation with waste production;
f) elimination of need for process water storage;
g) minimization of operating costs;
h) adaptability for future changes in standards;
i) applicability to other pollutant streams; and
j) robust construction for industrial operation.

A major benefit is a massive volume reduction in terms of the waste stream from the process. The operating parameters require a solvent volume amounting to between 2 and 4% of the process mass. If a nominal 10te.hr^{-1} is processed during a 10-hour period 100te of process water will be treated. The hold up volume of the system pipe work will be some hundreds of liters. This gives an average requirement substantially below 100 liters of extraction fluid. The external hold up volume where post processing of the extraction fluid may take place could lead to a parallel solvent reservoir of perhaps 200 liters to allow for any secondary processing. This will not necessarily change even if the unit is operated continuously for days or weeks.

In practice it has been identified that a wide range of oils are suitable as extraction solvent. It may be acceptable locally to use an existing waste oil stream to effectively avoid creation of an additional waste stream.

The process is viewed as a series of separate modules. The individual components are illustrated in the schematic presented below in Figure 1.
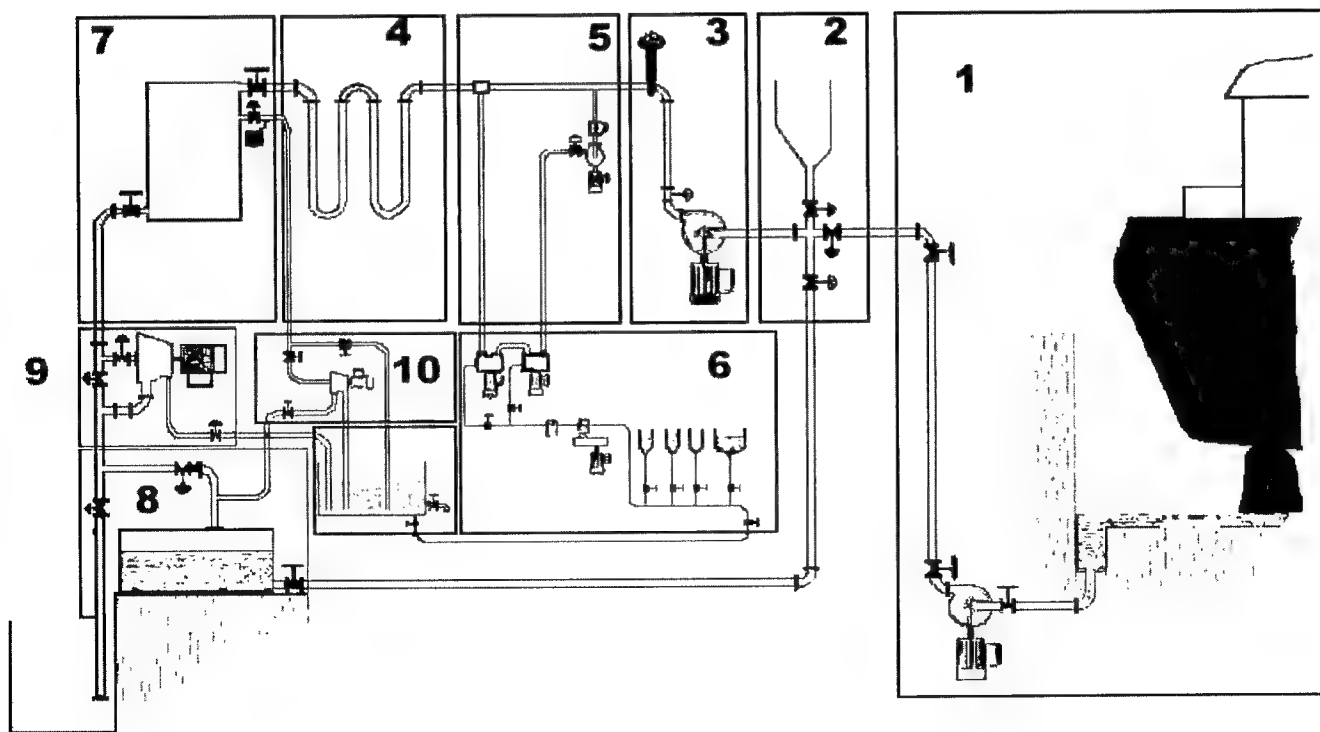
Figure 1. A schematic illustrating the components of the technology. See following text for legend.

The first module [1] includes a transfer pump to take the process stream from the source and will include primary screening to remove solids etc. The front end of the process unit will have a reservoir [2] to allow priming of the system prior to initiating treatment. This primary fluid stream will then be pumped [3] to the "reactor pipe work" [4]. A controlled fraction of the main flow is diverted [5] to the dosing system [6]. In this module, a concentrate is made with the extraction solvent being dispersed in the process liquid. The system will be capable of admitting any extraction solvent appropriate to the target pollutant.

The "reaction" module [4] maintains the dispersion of extraction solvent while the pollutant is extracted. The treated mixture then enters the separation module [7] where the solvent and cleaned water streams are separated. The water can go for discharge [8] or "polishing" [9] according to local quality standards. The oil stream is collected [10] for reuse, treatment or disposal according to local requirements. The solvent collection module can include secondary processing, recycling or simple discharge facilities.

PROTOTYPE PERFORMANCE

The technology has been proven to operate in an industrial environment with the ability to reduce TBT levels from $2mg.l^{-1}$ to $200ng.l^{-1}$. The use of repeat extraction modules will give progressive further reduction with no effective increase in waste volume produced. The estimated cost for each metric tonne of effluent treated is £4 (<$7).

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Minimization and Treatment of Shipyard Wastewater

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ABSTRACT

Shipyard operations generate significant quantities of wastewater apart from stormwater and sanitary wastewater. Efficient management of the wastewater streams results in reduction of costs, reduced liability, improved public image and environmental compliance. The pollution prevention options discussed in the paper follow the principle of source reduction which is the best alternative among all P2 options. The control techniques have been given for cleaning and degreasing operations, organic coating removal, surface treatment and plating operations. Use of aqueous cleaning solutions, process changes, efficient rinse systems, alternative process baths, numerous blasting techniques can be utilized for reducing the strength of the pollutants in the wastewater streams. Treatment would be required before final disposal into the waterbody to make water safe to aquatic life. Biological and physico-chemical treatment options are available to treat shipyard process wastewaters and bring the pollutants below the discharge standards.

INTRODUCTION

The shipbuilding and ship repair industry generates significant quantities of wastewater from various operations. Some of the major operations that generate wastewater are vessel cleaning operations, water used for cleaning the equipment, and water used in the processes (Kura, 1996a, 1996b). Apart from the washwaters, sanitary wastewater is generated at various restrooms and portable bathrooms within shipyards. A typical shipyard with dry-dock capability can generate as high as 7 million gallons of wastewater in addition to sanitary wastewater and stormwater. Such an enormous quantity calls for efficient management of shipyard wastewaters. Management techniques such as source reduction, waste minimization, control, treatment etc. can be effectively utilized in the

reduction of waste strength. This paper is the compilation of the available literature that relates shipyard wastewater minimization and treatment options.

WASTE MINIMIZATION

Waste minimization options are adopted more for process waters than for stormwater or sanitary wastewater because the reduction in toxicity, strength, and others is required in case of process waters. Control technologies can be adopted to minimize the strength of the waste streams coming out of various processes. These technologies or methods have been given in the following sections. Most of these methods follow the concept of source reduction which is the best alternative for pollution prevention.

Control Techniques for Cleaning & Degreasing Operations

In all of the control techniques that involve replacement of raw materials, care has to be taken to see that the quality of the replacement material satisfies the job requirements. In case of cleaning and degreasing operations, the solvent should have excellent solvency for a broad range of organic materials particularly oils and greases (EPA, 1994a). The solvent should preferably be non-flammable, non-corrosive, low toxicity, low heat of vaporization i.e., a high vapor pressure that allows evaporative drying of cleaned parts, and chemical stability. The chlorinated degreasing solvents have been extensively used in shipbuilding industry as they satisfy all the properties. The key chemicals of importance are methylene chloride (DCM), perchloroethylene (PCE) trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA). The chlorinated solvents are also highly mobile in soil and ground water and are common ground water contaminants.

There are two viable options that can be adopted for minimizing the waste in cleaning and degreasing operations: alternative cleaning solutions and process changes.

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Alternative Cleaning Solutions

Cleaning and degreasing can be broadly grouped as chemical, electrochemical, or mechanical in nature. The chemical properties possessed by a cleaner or solvent determine whether the cleaner or solvent acts by displacing, dissolving, or in some way chemically altering the contaminant on a substrate and hence causing its removal. Described below are chemical alternatives to chlorinated solvents that can be used to reduce waste in cleaning and degreasing operations.

Aqueous Wash Systems

Aqueous cleaning systems, or parts washing systems have been used for years to remove salts, rust, scale, and other inorganic soils from ferrous metals. Aqueous cleaning systems can include alkaline solutions and detergents to enhance their soil removal capabilities or consist of solely hot water washes. These systems are often used with pressurized sprays, agitation, ultrasonics, filtration, heat, or some other physical process to further provide effective cleaning.

Aqueous cleaners are mixtures of water, detergents, and other additives that promote the removal of organic contaminants. Some additives of aqueous cleaning systems include synthetic detergents and organic surfactants, saponifiers, acids and alkalies, and corrosion inhibitors. The combination of additives selected alter the foaming, wetting and soil removal properties of the solution. Detergents and surfactants are the surface-active agents that emulsify insoluble solids into solution. Saponifiers change water insoluble fats and fatty acids into water soluble soaps. Oxidants may be added to loosen rust and stains for easy removal. Depending on the requirements of subsequent operations, rinsing may be required to remove residual films left by these additives in the cleaning process.

Semi-aqueous Cleaning Systems

Semi-Aqueous cleaners comprise a group of cleaning solutions that are composed of natural or synthetic organic solvents, surfactants, corrosion inhibitors, and other additives. Semi-aqueous cleaners are designed to be used in process equipment much like that used with aqueous cleaners. The commonly used semi-aqueous cleaners include water-immiscible types (terpenes, high-molecular-weight esters, petroleum hydrocarbons and glycol ethers) and water miscible types (ketones, esters, and organic amines). One water miscible solvent, N-methyl-2-pyrrolidone (NMP), commonly used for large scale cleaning and paint removing which can be most suitable for shipyards.

Petroleum Hydrocarbons

Petroleum hydrocarbons are available in two grades, the basic petroleum distillates the older ones which were available many years before chlorinated solvents attained popularity. The other one is the speciality grade of synthetic paraffinic hydrocarbons, the most recent technologies which have high solvencies for many hard to clean organic soils, including heavy oil and grease, tar, and waxes. In addition they have low surface tensions which allow them to penetrate and clean small spaces. Petroleum hydrocarbon cleaners are compatible with most metals and plastics and with some elastomers.

Process Changes

The process changes result in reduction of contaminants in the process wastewaters. Some of the viable process changes are

- Automated aqueous cleaning
- Aqueous power washing
- Ultrasonic cleaning

Automated Aqueous Cleaning

Automated aqueous cleaners use aqueous cleaning solutions instead of solvents to achieve high quality cleaning. These automated machines also have features for significantly reducing the amount of wastewater generated. These machines remove some of the contamination that comes out from the parts being cleaned into the cleaning solution. The cleaning solution can then be recirculated for cleaning several times.

Aqueous Power Washing

The Aqueous power washing is similar to the automated aqueous washer in that it combines innovative process technology with the use of an aqueous cleaning solution. Unlike the automated washer which has a

continuous operation, most power washers are batch units. The power washer is most suitable for larger parts and is done by blasting from all sides with water or cleaning solutions in an enclosed chamber.

Ultrasonic Cleaning

Ultrasonic cleaning makes use of cavitation in an aqueous solution for greater cleaning effectiveness. In ultrasonic cleaning, high frequency sound waves are applied to the liquid cleaning solution. These sound waves generate zones

of high and low pressures throughout the liquid. These pressures and temperatures loosen contaminants and perform the actual scrubbing of the ultrasonic cleaning process.

The oily and greasy residue can also be removed by steam cleaning process. Heat accelerates emulsification, breakdown, and removal of caked-on dirt and grease. High temperature is maintained on the surface long enough for the steam to vaporize or liquefy the oil, grease, or dirt. This process reduces the amount of hazardous waste and hazardous air emissions generated in solvent degreasing. The wastewater stream generated can be easily treated at the treatment plant eliminating complications due to presence of toxics. Another method is the mechanical cleaning process to reduce waste production and eliminate potential safety problems with the handling and usage of toxic, ozone depleting, and often flammable solvents. Brushing, grinding, polishing, and sanding are some of the mechanical cleaning procedures adopted for this purpose. The mechanical cleaning process significantly reduces the amount of wastewaters/hazardous waste generated compared to chemical stripping and also reduces the treatment and disposal costs.

Control Techniques for Organic Coating Removal

Solvent strippers have been widely used for industrial coating removal for many years. The solvent strippers can remove a range of organic coatings at room temperatures without attacking metal substrates. Acidic solvent stripper typically include phenol, formic acid, and methanol mono-ethanol amine in the formulation in addition to the methylene chloride present in the ordinary solvent strippers. Methylene chloride removes the coating mainly by causing it to swell and then lift off the substrate. Because of the small size of the methylene chloride molecules, they penetrate beneath the coating surface to the substrate and cause the film to swell and lift off the substrate. The coating presents a bubbling and blistering surface, which signifies that the surface is ready for scraping or flushing.

Cleaner technologies are based on the physical removal of coatings to replace the use of solvent strippers. The difference in physical properties between coating and substrate is used for removal of coating. There are three general physical principles that can be adopted to replace solvent strippers (EPA, 1994c) and are

- Abrasive blasting technology
- Cryogenic technology
- Thermal technology

The nine available cleaner technologies based on these physical methods are plastic media blasting, wheat starch blasting, burn off coating removal, molten salt coating removal, sodium bicarbonate wet blasting, carbon dioxide cryogenic blasting, high-pressure water blasting, medium-pressure water blasting, and liquid nitrogen cryogenic blasting.

There has been increasing focus on tributyl tin as it is highly toxic. The standards exist only in the state of Virginia. Appropriate treatment technology has not been identified yet for wastewater containing tributyl tin. However, some BMPs (Best Management Practices) like cleaning of the dry dock and marine railway carriages before launching operations to eliminate the contamination of the waterways by tributyl tin compounds, ensuring proper enclosure of open blasting operations near the waterways to contain the spent abrasive media and the paint chips etc., are being followed to minimize the contamination of the wastewater stream by tributyl tin.

Control Techniques for Surface Treatment and Plating Operations

A wide variety of materials, processes, and products are used to clean, etch, and plate metallic and nonmetallic surfaces. Typical metal finishing processes include plating, anodizing, stripping, etching, degreasing, cleaning, tooling, buffing, grinding, polishing and other finishing steps. Some examples of the plating baths are nickel, tin, zinc, copper, cadmium, and gold baths. The process steps that generate wastes include plating, anodizing, etching, stripping, and rinsing steps. Wastes include spent baths, cleaning baths, and contaminated rinse water. The control techniques for surface treatment and plating operations can be categorized into two groups: process bath changes and rinse systems.

Process Baths

Source/waste reduction at the process-bath level can be established by material substitution, bath life extension, and/ or drag-out reduction. Material substitution options include modifying the chemistry of the process baths or replacing the chemicals used for a given process. Because process bath chemistries vary widely from plant to plant, these options are described below only in general terms.

Deionized water can be used to replace tap water for process bath makeup and rinsing operations. Natural contaminants found in tap water (e.g., carbonates, phosphates, etc.) can reduce the rinse water efficiency, minimize the potential for drag-out recovery, and increase the frequency of changing the process bath.

Converting to non-cyanide baths can simplify wastewater treatment, saving the cost of treatment chemicals and reducing sludge generation. Replacement chemistries are available for most cyanide containing process baths, with the exception of copper strike baths used for copper plating. This is an electrolytic process and is similar to cyanide based plating. Alkaline non-cyanide processes operate in pH of 8.8 to 9.8 compared to the pH of 13 to 14 for the cyanide process. Alkaline non-cyanide copper plating solutions eliminate cyanide from rinse water and sludge generated during waste treatment of the rinse water. Non-cyanide baths contain one-half to one-quarter as much copper as full strength cyanide processes, resulting in lower sludge volume generation rates. The sludge from waste treatment of cyanide bearing rinse water can be particularly difficult to dispose of because of residual cyanide content, which is regulated by RCRA to a maximum of 590 mg/kg of total cyanide and 30 mg/kg of cyanide amenable to chlorination. By eliminating cyanide from rinse water, compliance with cyanide regulations in wastewater discharges is ensured. Rinse water from alkaline non-cyanide copper plating only requires adjustment to precipitate copper as the hydroxide. This eliminates the need for a two-stage chlorination system from the waste treatment system and avoids the use of chemicals such as chlorine and sodium hypochlorite.

Rinse Systems

The greatest amount of wastes generated by the metal finishing operations comes from the treatment of wastewater resulting from rinsing operations required after the plating, stripping, and cleaning processes. The use of most wastewater treatment chemicals depends on the volume of wastewater generated. Therefore, it is important that rinse water usage be reduced in order to minimize waste generation in the metal finishing industry. Rinse water usage may be reduced by improving the rinsing efficiency and/or by controlling the water flow rate.

Rinsing efficiency may be improved by providing enough turbulence between the workpiece and the rinse water, sufficient contact time between the workpiece and the rinse water, and a sufficient volume of water during contact time. However, the last strategy causes the use of significantly more rinse water than required.

To improve the turbulence between the workpiece and the rinse water, spray rinsing or rinse water agitation systems may be used. Spray rinsing uses between 15 and 25 % of the volume of the water that a dip rinse system uses. However, it is not applicable to all metal finishers because the spray rinse may not reach all parts of certain work pieces. Spray rinse systems may be used along with dip rinse systems

(immersion rinse systems) as a first rinse step after the work pieces are removed from the process tank. This removes most of the drag-out before the workpiece is submerged in the dip rinse tank. Spray rinses can also be installed above the heated process tanks with rinse water volume less than or equal to the water loss resulting from evaporation. This allows the drag-out and rinse water to drain directly to the process bath, thus replenishing the bath solution.

Agitation between the workpiece and the rinse water can be achieved by using forced air or forced water systems. In these systems, air or water is pumped into the immersion rinse water tank. Air agitation is thought to provide the best type of turbulence for removing process bath chemicals. An air sparger at the bottom of the rinse water tank is frequently used for forced air systems.

The use of multiple-stage rinse tanks can increase contact time between the workpiece and the rinse water, thus improving the rinse efficiency. A countercurrent multiple-stage rinse tank system can also reduce the amount of water usage (by 90 % when compared with a conventional single-stage rinse system). In a multistage countercurrent rinse system, the rinse water flow moves in an opposite direction to the workpiece flow. The disadvantages of multistage countercurrent rinse systems are that more process steps, additional equipment, and greater work space are required.

Rinse water usage can also be reduced by controlling the flow rate. Flow restrictors can be used to limit the volume of the rinse water and maintain a constant flow of fresh water into the system. A conductivity or pH meter can also be used to control the flow of fresh water into the rinse system by monitoring the level of dissolved solids or pH in the rinse water. When the concentration or pH reaches the preset maximum level, the probe can activate a valve which opens to allow an additional flow of fresh water into the rinse water system.

There also exist the recycling and resource recovery technologies to the metal finishing operations. To reuse or recovery a waste stream for another process and to recycle rinse water, the waste stream must be separated from other wastes that may interfere with the reuse or recovery process. Therefore, implementation of recycling and resource recovery techniques will generally require process piping modifications and additional storage tanks to provide the necessary segregation of materials.

After the rinse water becomes too contaminated for the original process, it may be useful for other rinsing operations in which the purity of the water is not crucial to the process. For example, the effluent from a rinse tank following an

acid cleaning bath can be reused as influent water to a rinse tank following a basic cleaning bath. Not only is water usage reduced by 50 % (assuming both rinse tanks require the same water flow rates), but at the same time rinsing efficiency is improved, owing to the neutralization reaction that reduces the concentration of alkaline chemicals. Neutralization reactions can also reduce the viscosity of the alkaline drag-out film.

Acid cleaning rinse water effluent can be used as rinse water for work-pieces that have gone through a mild acid etch process. Rinse water from a final rinse, which is less contaminated than other rinse waters, can be used as influent for other rinsing operations that do not require high rinse efficiencies.

Alkaline or acidic spent process chemical baths can be used to adjust pH during waste treatment. However, they should not be used for final pH adjustment since they often contain high concentrations of metals.

Because of the increased regulatory requirements on handling and disposal of wastes containing metals, and the subsequent increase in treatment costs, it has become more economical to recover metals and metal salts from process baths. Metal recovery may be used in two ways:

- Recovered elemental metals can be sold to a metal reclaimer
- Recovered metal salts can be recycled back to the process baths

The available techniques for recovering metals and metal salts are evaporation, reverse osmosis, ion exchange, electrolysis, and electro dialysis (closed loop [Fig. 1] and open loop [Fig.2] systems).

TREATMENT

The treatment of the wastewater is generally carried out on-site owing to substantial quantities of wastewater generated in the shipyard. A typical shipyard may generate up to seven million gallons of wastewater from process/washwater streams. This figure does not include stormwater and sanitary wastewater. Treatment of wastewater involves preliminary treatment, primary treatment followed by secondary treatment. The secondary treatment can be chosen from two alternatives: biological treatment and physico-chemical treatment. These treatment options have been discussed in the following sections.

Biological Treatment

Suspended solids in a shipyard wastewater can be of two types: settleable and non settleable. The former can include grit and other discrete particles that can be easily removed in a grit chamber. Settleable organic particles can be removed in a primary sedimentation tank (La Motta and Kura, 1997). The non settleable particles can be colloidal and dissolved particles, both organic and inorganic. The organic biodegradable fraction can be removed using conventional biological treatment processes, while the inorganic colloidal solids need some form of flocculation to become settleable.

Based on the wastewater characteristics of a typical shipyard, the following treatment processes are deemed necessary to obtain concentrations below discharge limits: preliminary treatment, primary treatment, secondary biological process, secondary settling, effluent filtration, adsorption of non biodegradable organics, final effluent disinfection and sludge treatment.

Preliminary Treatment

The first unit process in a shipyard wastewater treatment plant would be the grit chamber, preferably aerated. In shipyards grit would be composed of sand, metal chips, or other heavy discrete particles generated in metal surface preparation. Grit must be removed because its inclusion within the system can abrade mechanical equipment and settle out in pipelines, channels and conduits, and interfere with biological treatment of sludges.

Two common types of grit collection devices are (Kiely, 1997) the helical flow aerated grit chamber and the horizontal flow grit chamber.

Primary Treatment

Wastewater from barge cleaning, bilge wastes, process waters and sanitary wastewater have concentrations of oil and grease typically between 100 and 150 mg/L. The general discharge limit for oil and grease is 15 mg/L. Hence, an oil-water separator is usually employed to separate out the oil from the wastewater. This separated oil can be sold to outside customers for use as fuel.

Secondary Treatment

Biodegradable organics contained in shipyard wastewater can be easily removed using any of the conventional

biological treatment processes or their combination. Several of the available alternatives, namely, suspended growth processes (conventional activated sludge, extended aeration) and fixed-film processes (trickling filters, rotating biological contactors, aerobic fluidized beds) could be selected. The final selection, however, should be based on the review of each of the treatment options in accordance with the wastewater characteristics of the shipyard.

The two common methods of treatment using microorganisms are the activated sludge process and trickling filters. The main methodologies of these units have been described in the following sections. Procedures for unit design, design parameters, and other details can be found in standard wastewater treatment literature (Metcalf & Eddy, 1991; Qasim, 1994).

The Activated Sludge Process

The activated sludge process uses suspended bacteria to assimilate the organic matter present in the waste stream for cellular growth, and in that way, it transforms dead dissolved and colloidal organic matter into live biomass. As the microorganisms grow and are mixed by the agitation of the air supplied to the reactor, the individual microorganisms clump together to form an active mass of microbial floc called "activated sludge" (Qasim 1994). Once the microbial floc is formed it becomes settleable and thus can be separated from the liquid in the sedimentation tank. A significant fraction of the biomass separated at the settling tank is recycled back to the aeration unit to maintain the proper food-to-microorganism ratio, and the excess sludge is wasted to the sludge treatment system.

Although there are several process modifications, the most common type of activated sludge is the compete mix aeration system. The influent and the returned sludge are mixed and applied at several points along the length and the width of the aeration basin. The contents are completely mixed by the aeration system so that the biological oxygen demand is satisfied by the oxygen supplied throughout the tank.

The activated sludge process can be easily employed for treating shipyard wastewater as it does not occupy much space. The treatment process can be carried out in floating tanks placed on a barge. The complete mix system may require heating to enable proper temperature conditions for the microbes to work effectively.

Trickling Filters

The trickling filter consists of a bed filled with crushed stones or synthetic media, with their surface coated with a biological film. Wastewater is applied intermittently on the filter surface by means of a self propelled rotary distribution arm. The dissolved or colloidal organic substances are removed by the attached biological film, which grows in thickness as bacteria, protozoa and other microorganisms multiply within the film. The microorganisms living at the film surface are exposed to high concentrations of oxygen and substrate, while those developing at the base may receive very low levels of oxygen and substrate. When the film thickness is excessive, the microorganisms living at the base may starve and die-off, the film detaches, and a new growth cycle starts.

The TF process efficiently treats industrial wastes having a high percentage of soluble, small molecule organic material, and readily removes suspended and colloidal organics by the combined process of flocculation, adsorption, and enzyme complexing (WEF, 1991). The versatility of trickling filters towards variations in the wastewater characteristics makes them useful for treating shipyard wastewater as the wastewater from various operations varies with factors like different types of vessels being cleaned, different kinds of processes being employed at times owing to their intermittent nature, and others. Also, the ability of TFs to treat low-strength streams can be utilized for treating shipyard wastewater.

Tertiary Treatment

As part of tertiary treatment, the treatment plant could have filtration to further remove suspended solids, and adsorption, to remove non biodegradable organic compounds that may be toxic to aquatic life. The filtration of effluents from wastewater treatment processes is a relatively recent practice (Metcalf & Eddy, 1991), used for achieving supplemental suspended solids removal from biological or chemical treatment processes.

Carbon adsorption is an advanced wastewater treatment method used for the removal of refractory organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals (Metcalf & Eddy, 1991). Filtration of effluents through granular activated carbon beds must be preceded by sand filtration to protect the carbon particles against significant pressure loss, channeling or blockages. If powdered activated carbon (PAC) is used, it is usually added to the activated sludge aeration basin, so that biological oxidation and physical adsorption occur simultaneously.

Physico-chemical Treatment

The main difference between the biological treatment plant and physico-chemical treatment is that the latter does not rely on bacteria to remove organic matter from wastewater.

To remove colloidal particles, both organic and inorganic, chemical addition is required. Coagulants added to the wastewater stream will destabilize the colloidal suspensions and floc formation will take places in a flocculator. Dissolved organic substances must be removed by adsorption in activated carbon filters. Thus, the sequence of treatment units in a typical physico-chemical shipyard treatment plant would be the following: preliminary treatment, chemical addition, flocculation, dissolved air flotation, effluent filtration, adsorption of organics, final effluent disinfection and sludge treatment. This section will only describe the new units needed in physico-chemical treatment, namely, flocculation and dissolved air flotation.

Flocculation

The purpose of flocculation is to form settleable particles from the destabilized colloidal particles. The flocculator is a separate reactor, with a holding time of around 30 minutes, where the wastewater is agitated gently with paddles rotating at a velocity between 1.3 and 3.3 ft/s. This gentle agitation will promote particle growth so that the larger floc particles will be easily separated by gravity or by flotation.

Dissolved Air Floatation

The addition of chemical coagulants (alum, polymers) will also destabilize emulsified oil particles and promote the formation of oil droplets; these larger particles can be easily dragged to the surface by the small air bubbles generated in the flotation unit. Dissolved air flotation (DAF) is a wastewater treatment process in which oil, grease, and other low density suspended matter are removed from a waste stream. Ekenfelder (1980) reports that oil tanker ballast water with an oil concentration of 133 mg/L was successfully treated by dissolved air floatation and the addition of 100 mg/L of alum and 1 mg/L of polymer; the effluent oil concentration was reduced to 15 mg/L.

There are three modes of injecting air bubbles into the waste stream: recycling, total pressurization, and partial pressurization. Total pressurization is used in small installations, whereas in larger units, recycle or partial pressurization is usually selected (EPA 1973a, 1973b). With wastewater containing emulsified oil or grease, chemical conditioning is necessary to break the emulsion and form a floc to absorb the oil or grease. The particle growth preceding floatation contributes to the effectiveness of the floatation process. Therefore, when chemical addition is used to break up the emulsion, a flocculation chamber is generally used preceding the floatation process.

In the case of shipyard wastewater, excluding storm water runoff, treatability studies should be conducted to determine

not only the design parameters for the DAF unit, but also to determine whether chemical treatment and flocculation are needed to improve the DAF unit efficiency.

A typical treatment train for wastewater treatment in shipyards is illustrated in Figure 3. Table 1 gives the typical effluent characteristics after treatment and before discharge into the water body.

Other Treatment Options

The treatment procedures described in this section give options to treat either one or a group of pollutants that may occur in the wastewater streams in a shipyard. Some of these options can be integrated with the conventional biological or physico-chemical treatment after assessing their compatibility to these treatment methodologies.

Sodium Nitrite is used for marine steam boiler maintenance operations like hydroblasting cleaning, hydrostatic pressure testing, lay up , and rinsing. The addition of sulfamic acid to wastewater effectively removes sodium nitrite by reducing nitrites to form sodium bisulfate, diatomic nitrogen, and water.

Ferrous sulfate/Sodium sulfide process is used to remove heavy metals from wastewater through precipitation at normal or alkaline pH. Ferrous and sulfide ions act together to reduce hexavalent chromium to trivalent chromium to form a precipitate. The ferrous and sulfide precipitate further removes suspended and dissolved metals through coagulation and flocculation. Sodium hydroxide can also be used for heavy metal precipitation. Sodium hydroxide forms a precipitate that removes heavy metals through coagulation and flocculation similar to ferrous sulfate/sodium sulfide process. Addition of sulfuric acid neutralizes the wastewater prior to discharge.

Activated carbon beds are used to remove toxic organic compounds from wastewater. Costs of handling and disposal of activated carbon waste streams can be high. Carbon regeneration through thermal destruction/scrubbing system destroy organic contaminants and regenerates the carbon for reuse resulting in reduction in disposal costs and also purchase of fresh carbon.

The ultraviolet(UV) oxidation process destroys dissolved organic constituents through chemical oxidation process using UV and hydrogen peroxide. UV light also catalyzes the breakdown of hydrogen peroxide to produce hydroxyl radicals, which are powerful chemical oxidants. Oxidants react with organic matter to produce harmless carbon dioxide, halides and water byproducts. Table 2 gives a summary of the minimization and treatment options

Table 1. Effluent characteristics of a typical wastewater treatment plant effluent

Parameter	Concentration, mg/l
Oil and Grease (O&G)	<5.0 to 8.0
Chemical Oxygen Demand (COD)	39 to 144
Total Suspended Solids (TSS)	6 to 40
Phenols	<0.005 to 0.024
pH	Around 7.0
BTX	BQL
Purgeable Halocarbons	BQL

MQL = Minimum Quantification Level - USEPA Region VI NPDES; BQL = Below MQL

available for shipyard wastewater.

CONCLUSIONS

Various shipyard operations like vessel cleaning, pipeshop operations, solvent cleaning and degreasing and others generate huge quantities of wastewater. The quantities from the process/washwaters in a typical shipyard can be as high as seven million gallons in a year. Such high quantities invariably draw the attention of the shipyard environmental managers to reduce the waste streams.

Pollution prevention is the best sought out method for reducing pollution. Many options are available for reducing the extent of pollution from shipyard processes most of them being source reduction methods. Various methods like process changes, replacement of solvent strippers, alternative cleaning solutions, cleaner abrasive media, efficient rinse systems, effective reuse and recycling options including evaporation, reverse osmosis, electrolysis, and others are viable source reduction methods.

Looking into the characteristics of wastewater from various processes, two alternatives for treatment of oil & grease, COD, TSS, and others were discussed. The biological treatment can employ either the activated sludge process or the trickling filter concept in the secondary treatment. On the other hand, physico-chemical treatment does not involve treatment by microorganisms but will require additional physical processes like flocculation and dissolved air floatation. Implementation of pollution prevention technologies in shipyard could result in cost benefits, regulatory compliance, and increased public image apart from reduction in liability.

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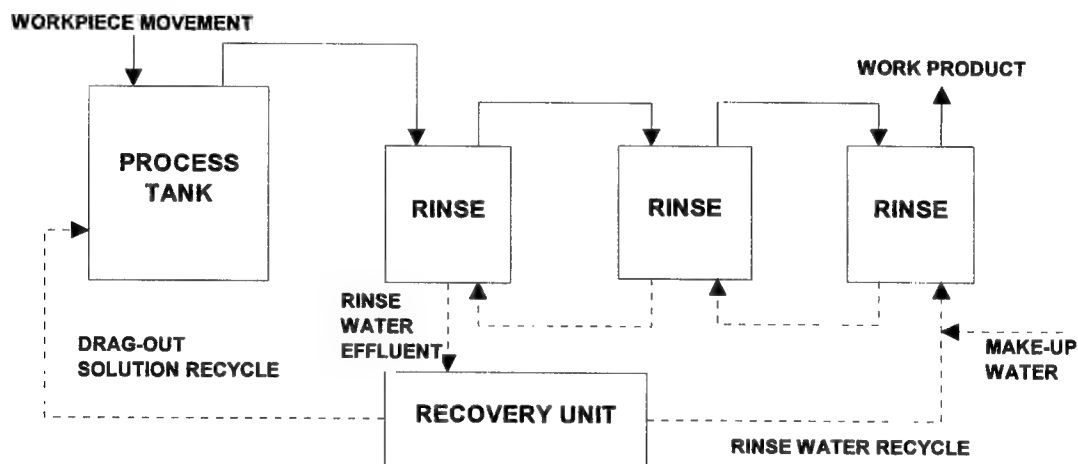
Figure 1. Electro-Dialysis Closed Loop System
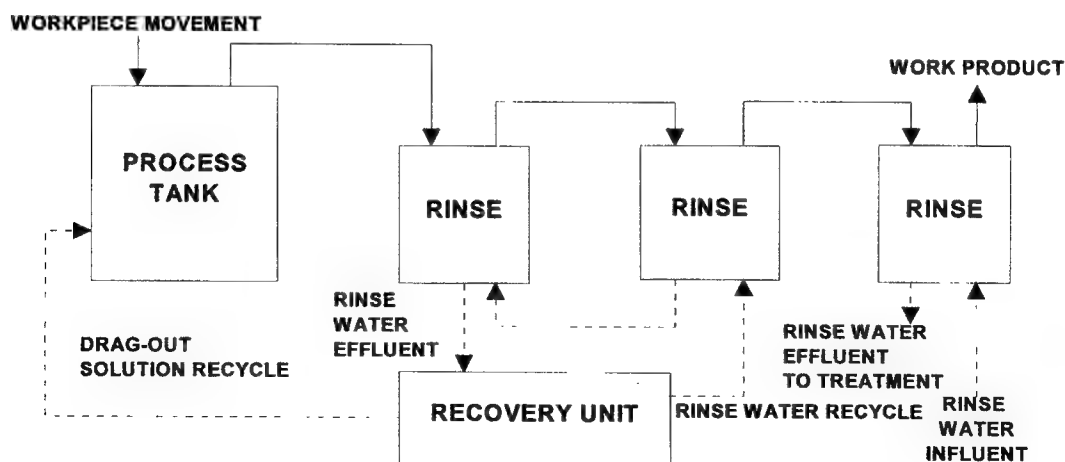
Figure 2. Electro-Dialysis Open Loop System

Process wastewaters and washwater

```
┌─────────────────┐     ┌──────────────────┐     ╭──────────╮
│  Sedimentation  │     │ Primary Biological│     │ Primary  │
│  and Stripping  │ ──► │     Reactor       │ ──► │ Clarifier│
│     of Oils     │     │ (Heating/Aeration)│     ╰──────────╯
└─────────────────┘     └──────────────────┘
```

Recovered oil is sold to outside customers

```
┌──────────────────┐     ┌──────────────┐     ┌──────────────┐
│Secondary Biological│    │ Spent Carbon │     │  Double Bag  │
│     Reactor       │ ◄── │     Tank     │ ◄── │    Filter    │
│(Heating/Aeration) │     └──────────────┘     └──────────────┘
└──────────────────┘
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╭──────────╮     ┌──────────────┐     ┌──────────────────┐
│Secondary │     │  Single Bag  │     │ Activated Carbon │
│ Clarifier│ ──► │    Filter    │ ──► │  Final Polisher  │
╰──────────╯     └──────────────┘     └──────────────────┘
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                                    ┌──────────────┐
                                    │Cartridge Filter│
                                    └──────────────┘
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Discharge to water body
through outfall

Figure 3. Typical Wastewater Treatment Train for Shipyards

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Table 2. **Summary of various treatment and waste minimization options available for shipyards***

Treatment	Description	Costs
Sodium Nitrite Removal	Sodium Nitrite is used for marine steam boiler maintenance operations like hydroblasting cleaning, hydrostatic pressure testing, lay up, and rinsing. The nitrite level in the wastewater prohibits discharge of wastewater. The addition of sulfamic acid to wastewater effectively removes sodium nitrite by reducing nitrites to form sodium bisulfate, diatomic nitrogen and water.	Annual savings are $10 million.
Heavy Metals Removal	1. Ferrous sulfate/ Sodium sulfide process is used to remove heavy metals from wastewater through precipitation at normal or alkaline pH. Ferrous and sulfide ions act together to reduce hexavalent chromium to trivalent chromium to form a precipitate. The ferrous ions acts with the sulfide, aiding in the reduction of chromium at neutral or alkaline conditions. The ferrous and sulfide precipitate further removes suspended and dissolved metals through coagulation and flocculation. Sodium hydroxide may also be added to remove heavy metals.	Capital costs are around $250,000, other costs being negligible.
	2. Precipitation and microfiltration use a combination of treatments on a variety of wastes. Chemical precipitation of heavy metals is the first step in this process. Precipitates larger than 0.1to 0.2 micron are filtered in a tubular fabric crossflow filter. Concentrate is dewatered using conventional process. In microfiltration wastes are pumped into polyester tube that produces a high quality filtrate and removes all particles larger than 0.1 to 0.2 micron. Metals are removed by precipitation in a reaction tank by adjusting their pH. Oil and grease are removed by adding adsorbents. Organics and solvents can be removed by AC, or powdered ion exchange resins	Capital Cost is $1.00 - $2.00 per gallon per day; O&M cost is $1.00 - $2.50 per 1,000 gallon
Oxidation	1. The laser-induced photochemical oxidative destruction (LIPOD) is a method to photochemically oxidize organic compounds in wastewater. The oxidation process uses a UV laser to excite organic compounds in the presence of an oxidant to initiate a chain oxidation reaction.	Capital Costs are $25,000 - $60,000;
	2. Wet Air Oxidation (WAO) destroys toxics in wastewater by breaking down in simpler components. Process is based on the knowledge that organics will oxidize at relatively low temperatures provided oxygen and proper operating pressures are maintained. Applicable to wastewaters containing organics and oxidizable inorganics. Used to oxidize sewage sludge, regenerate spent AC, and treat process wastewaters.	Capital cost is $12 million; O&M cost is $480,000/yr.
	3. The ultraviolet(UV) oxidation process destroys dissolved organic constituents through chemical oxidation process using UV and hydrogen peroxide. Contaminants absorb UV light thereby changing their chemical structure or become more reactive with chemical oxidants. UV light also catalyzes the breakdown of hydrogen peroxide to produce hydroxyl radicals, which are powerful chemical oxidants. Oxidants react with organic matter to produce harmless carbon dioxide, halides and water byproducts.	Capital cost - $339,000; O&M cost is $100,000/yr.

Category	Description	Cost
Oil/Water Separation	1. Reverse Osmosis (RO) uses membrane separation systems to remove inorganic salts as well as some organic solvents from wastewater. Reverse osmosis occurs when pressure is exerted on the contaminated solution causing water to flow from the contaminated solution to pure water. Ultra-filtration (UF) is pressure driven membrane filtration process which is used to separate and concentrate macromolecules and colloids from wastewater. UF is a stand alone process or can be used with RO. Used to treat sanitary landfill waste containing organic and inorganic chemicals, solvent-water mixtures, oil-water mixtures.	Capital cost is $450,000 for a loading of 40,000 gpd; O&M cost is $194,800/yr.
	2. Oil/water separators are self contained, automatic treatment systems used for treatment of oily wastewaters. Units use a coalescing pack to promote oil globule agglomeration to enhance conventional gravity separation process. Gravity separation takes advantage of density difference between oil and water. Formation of oil globules is promoted so that their buoyancy increases and they rise to the surface at a faster rate.	Capital cost is $30,000 for 10 gpm unit; O&M cost is $96,400/yr including labor.
	3. Bilge and Oily Wastewater Treatment System (BOTWS) separates oil from contaminants found in bilge waters. BOTWS is a stationary system. The bilge water is transferred to a large equalization tank equipped with skimmer to remove free oil. After sufficient residence time, the water fraction is selectively removed and fed through a plate coalescer for removal of free oil. The water is fed into the chemical treatment chamber where sodium hydroxide and anionic polymer are added and mixed. This results in breakdown of emulsion and precipitation of heavy metals. The heavy metals are removed in an induced-air flotation unit.	Capital costs are $1,400,000; O&M cost is $155,000/yr.
Biological Treatment	1. Bio Trol BioAccelerator uses microbes to degrade contaminants in wastewater. The pH is adjusted and inorganic nutrients are added. If necessary the water is heated to optimum temperature. The heated water flows into a multiple cell, submerged, fixed film bioreactor. The cell is filled with packing material to which the microbes adhere. For aerobic conditions air is supplied by fine bubble diffusers at bottom of cell.	Capital cost is $150,000; O&M costs are $21,300/yr including labor.
	2. Powdered Activated Carbon (PAC) combines biological treatment with adsorption method. Typically, PAC contact wastewaters in an aeration basin. Biomass removes biodegradable organic contaminants through biological assimilation and carbon physically adsorbs conventional and toxic organics. Applicable to end-of-pipe treatment of industrial wastewaters, combined municipal/industrial wastewaters, contaminated surface runoff and groundwater, and landfill leachates.	Capital costs are $100,000 - $300,000 for mobile units; O&M cost varies from $0.50 to $1.00 per 1,000 gallons.

Category	Description	Cost
Reuse	1. Secondary use of acids and alkalis as treatment chemicals in wastewater treatment for neutralization. Replaces treatment chemicals like sulfuric acid and sodium hydroxide in chromic reduction, cyanide oxidation, metal precipitation and neutralization processes.	Capital Cost is $14,112/yr; labor cost is $8,100/yr.
	2. Activated carbon beds are used to remove toxic organic compounds from contaminated groundwater, wastewater. Cost of handling and disposal of activated carbon waste streams can be high. Carbon regeneration through thermal destruction/scrubbing system destroys organic contaminants and regenerates the carbon for reuse.	Capital cost is $16,860/yr.
Recycling	1. Cutting fluid recycling system is based on the centrifugal removal of contaminants which will treat 60 to 300 gallons of cutting fluid per hour. Cutting fluid recycling systems incorporate filtration, centrifugation, pasteurization, oil skimming, and/or coalescence processes. The unit includes the following options: a self-cleaning centrifuge, a proportional mixer system, a heat exchanger, processing tankage, a clean coolant distribution system, and water deionizer.	O&M cost is $6,500/yr; labor cost is $2,200/yr.
	2. Washwater Recycling: A closed loop wash rack contains and treats wastewater generated from washing vehicles, construction equipment, and aircraft. A typical process flow for water recovery system comprises of a first unit separates free oil and dirt from wastewater. The second unit removes fine dirt particles and remaining hydrocarbons. The next unit stores the water in a holding tank for reuse.	Capital cost is $10,430/yr; O&M cost is $550/yr including labor.
Process Modification/ Material Substitution	1. Mechanical cleaning process reduces waste production and eliminate potential safety problems with the handling and usage of toxic, ozone depleting, and often flammable solvents. The mechanical work of cleaning operations include 1) Brushing, using wire or plastic brushes, 2) Grinding, using a rotating abrasive stone or disc, 3) Polishing and buffing, using a soft device like a fabric or fiber cloth, and 4) Sanding, using a fiber sheet embedded with sand or other mineral grit particles that removes surface dirt or loose paint.	Capital cost is $420; O&M cost is $1,468/yr; labor cost is $345,600/yr.
	2. Heat is primarily used in the steam cleaning process. Heat accelerates emulsification, break-down, and removal of caked-on dirt and grease. High temperature is maintained on the surface long enough for the steam to vaporize or liquefy the oil, grease, or dirt.	Capital cost is $5,000; O&M cost is $700/yr; labor cost is $7,800/yr.
	3. Uses sonic vibration to produce cavitation bubbles in liquid medium which removes contaminants.	Capital cost is upto $180,000.

* Various assumptions went into estimation of costs details of which can be obtained from the source: Naval Facilities Engineering Service Center, 1998, *Joint Service Pollution Prevention Technical Library.*

Using Ground Recycled Glass in Abrasive Blasting to

Reduce Shipyard Contamination

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ABSTRACT

Recent developments in the use of ground recycled glass as an abrasive blasting media show that the material is a viable substitute for commonly used slag and mineral abrasives. Because of its physical properties, density and angularity, ground glass offers distinct performance benefits. With no free silica and no heavy metals, the critical advantages to ground recycled glass are in the areas of environmental compliance, toxics and waste reduction, and worker safety.

Keywords: Abrasives, abrasive blasting, surface preparation, coating removal, ground recycled glass, industrial hygiene, shipyards, dry docks.

INTRODUCTION

As participation in recycling programs grows in North America, significant quantities of recycled glass are being generated beyond the capacity for bottle plants to absorb the material back into production. Hence, there is a strong need to develop new markets for recycled glass. For over ten years, glass processors have slowly introduced finely ground recycled glass into the abrasive blasting industry. Within the last three years, market acceptance of the use of ground recycled glass abrasives has grown sharply as new information is developed about the productivity, environmental and safety benefits of this technology. In 1999, NAVSEA listed the first ground recycled glass on its Qualified Products List (QPL) under its specification MIL-A-22262-B(SH), Abrasives, Ship Hull Blast Cleaning.

Recent test data, including a major study of abrasives by NIOSH, point to the fact that ground recycled glass offers a safer, productive alternative media for use in shipyards.

PROPERTIES OF GROUND RECYCLED GLASS

At an approximate bulk density of 80 lbs. per cubic foot and a Mohs hardness of 6.0, ground glass is an inert, amorphous material well suited to an abrasive media application. Processing systems are in place in several North American locations to produce consistently sized, angular to sub-angular grain sand from recycled glass. With proper grinding, drying, and screening, the finished product will be a clean, contaminant free sand-like material.

In stark contrast to commonly used mineral and slag abrasives, ground glass contains virtually no heavy metals. Insignificant quantities of contaminants from the recycling stream should be substantially removed during the manufacturing process. Achieving approval under the NAVSEA specification is proof that this media can meet demanding environmental specifications. NAVSEA test results indicated exceptionally low levels of chlorides, organics and conductivity in addition to the relative absence of 17 tested metals.

Because glass is amorphous, there is no crystalline structure to the silica or other ingredients of glass, nor can crystalline silica be created by simply breaking glass particles down to finer sizes. The

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absence of free silica in an abrasive media is a significant benefit, as OSHA, NIOSH and state industrial hygiene agencies continue to warn about the silicosis risks associated with blasting with silica sand and other abrasives containing free silica.

INDUSTRIAL HYGIENE

Recently NIOSH completed a three-year study {Evaluation of Substitute Materials for Silica Sand in Abrasive Blasting, NIOSH, Sep 1998, Report No. PB99105553, available from http://www.ntis.gov, http://www.cdc.gov/niosh/homepage.html or 800-553-NTIS} of a wide range of slag and mineral abrasives in an effort to evaluate the effectiveness and industrial hygiene of alternatives to silica sand for abrasive blasting. A summary of the study was published in the August issue of the *Journal of Protective Coatings and Linings*. After extensive performance and safety tests of 40 samples of 13 different types of abrasives, including crushed glass, the NIOSH report calls for fundamental re-consideration of the safety of abrasive blasting with most of the slag and mineral products commonly used. The findings of the study were striking in the occurrence and extraordinary concentrations of heavy metals present in airborne dust from blasting with copper, nickel and coal slags, as well as several other mineral abrasives.

For instance, the geometric mean concentration of all arsenic detection tests during copper slag blasting was $89.1\mu g/m^3$, 9 times greater than OSHA regulations allow. Similarly, the geometric mean concentrations of chromium detection test during nickel slag blasting was $811.8\ \mu g/m^3$, 62% higher than the OSHA PEL for chromium. As a result of finding these and many other high concentrations of hazardous health-related agents in slag and mineral abrasives, the NIOSH report recommendations include:

1. "In order to reduce the airborne concentrations of the eleven hazardous health-related agents, consider the use of crushed glass..."

4. "Given the potential exposures to multiple contaminants from both the abrasive, as well as the painted surface, worker protection programs should be expanded to address all potential metals (e.g. as opposed to the current

focus on worker lead protection programs)..."

6. "Evaluate the potential for correlations between the concentration of health-related agents in all virgin abrasives and in particular coal slag, copper slag, garnet and steel grit, and the resulting airborne concentrations, for use as a selection criteria."

ENVIRONMENTAL CONSIDERATIONS

The NIOSH report documents, from an industrial hygiene perspective, serious heavy metal concentrations in commonly used abrasives. Beyond risks to workers, these heavy metals may present unnecessary environmental risks as well. Detected total levels of heavy metals increased significantly in the airborne dust from abrasive blasting. Considering shipyard needs to manage and control spent abrasives, fugitive dusts, dry dock and shipyard storm water, and spills, the availability of an alternative media with no heavy metals can offer significant benefits to shipyard operations. Additionally, as federal agencies seek out the use of recycled and environmentally preferable products, provision of 100% recycled glass media offers unique solutions.

Because of its performance characteristics, ground glass also offers significant potential for waste reduction. Most blasting operations report using between 30% to 50% less media compared to copper slag abrasives. Less media consumed is less media requiring disposal. Notably, in some cases where the media is used on a clean, inert surface, the spent abrasive is used as a soil amendment or left on site, since there are no leachable heavy metals for concern. Otherwise, spent glass abrasives may be safely disposed of in landfills or asphalt plants, in accordance with applicable waste regulations.

PERFORMANCE ISSUES

Ground glass has its own set of unique performance characteristics. Because they are relatively lighter and sharper than common abrasives, ground glass abrasives perform very well in coating removal applications such as epoxies, alkyds and enamels, and especially thicker, softer or rubbery coatings. Conversely, because of glass' lighter density, removal

of harder or tougher coatings, heavy rust, or thick mil scale requires particular operator skills and approaches in order to be successful. While conventional abrasive blasting equipment can be used, attention must be given to properly setting air pressures and metered flow rates in using the abrasive.

Ground glass shows very little embedment in steel, and dust from blasting with it is lighter and easier to evacuate from the work area. Engineers and consumers of blasting services are concerned about the condition of surfaces, particularly steel, prior to coating. The amount of embedment, chlorides content, metals content and conductivity of abrasives are of concern because of the potential for rusting or other causes of coating failure. It is reasonable to assume that, regardless of operators' skill or diligence, risks for costly coating failures due to embedment, chlorides, conductivity, or traces of metals will be greatly reduced through the use of recycled glass abrasives.

Ground glass is unique in its ability to economically clean aluminum, brass, copper, and stainless steel with little to no substrate damage. Until the use of this type of abrasive, these types of surfaces had to be cleaned with garnet, baking soda, glass bead, walnut shells, or other media – all of which are several factors more expensive than ground glass. The light, aggressive nature of ground recycled glass allows for very productive cleaning without staining, warping, excessive profiling or surface damage. Properly used, ground glass shows strong advantages in "spot" and "sweep" blasting because it tends to be less damaging to surrounding painted areas, leaving smoother surfaces and more gradual feathered edges.

Shipyard engineers, specifiers and operators must have sufficient knowledge of project conditions to "pre-qualify" the types of abrasives allowed. In certain applications, such as those mentioned above, ground glass shows significant performance advantages. Ground glass has the potential to replace many slag and mineral abrasives for a range of common de-painting and rust removal tasks. In general abrasive blasting work, it is competitive in price and performance with these bulk abrasives. In the whole consideration, including environmental and worker safety aspects, ground glass abrasives can provide unique and distinct advantages for shipyard operations.

Further information about the Navy QPL listed ground glass abrasive, see http://www.trivitro.com. Because the development of abrasives markets is important to the future of recycling, the Clean Washington Center sponsored independent evaluations of ground glass abrasives. Test reports are available at http://www.cwc.org (click on "publications" and "glass.").

Environmental Enclosure Systems for Industrial Ship Applications to Prevent Emissions and Discharges

Douglas A Randall[1]

ABSTRACT

The Department of National Defense, Fleet Maintenance Facility on Cape Scott, in Halifax, NS is a large Industrial Ship Repair Facility that is owned by the Canadian Government and operated by the Navy. The facility has an ISO 9001 Quality Management Certification and has also achieved an ISO 14001 Environmental Certification. The facility has a work force of approximately twelve hundred people with a focussed role of maintaining the operational readiness for the Navy. The challenge to the facility is to protect the environment and conform to all the latest environmental regulations that have been legislated by all levels of government. Further to these regulations the Navy has also written guidelines that regulate the way the Navy does business with regards to the environment. Initially, the ship repair facility feared that the introduction of new environmental policies may put it out of business. This has not been the case, as on average only three percent of the total cost of the refit has been spent on protecting the environment during the refit process. It is important to note that the emphasis of the facility has been from the beginning to prevent the discharge of effluents into the marine aquatic environment.

INTRODUCTION

The DOD Fleet Maintenance Facility is a large Industrial Ship Repair Facility that is owned by the Canadian Government and operated by the Navy. We have an ISO 9001 Quality Management Certification and have also achieved an ISO 14001 Environmental Certification. We have a work force of approximately twelve hundred strong with a focussed role of maintaining the operational readiness for the Navy.
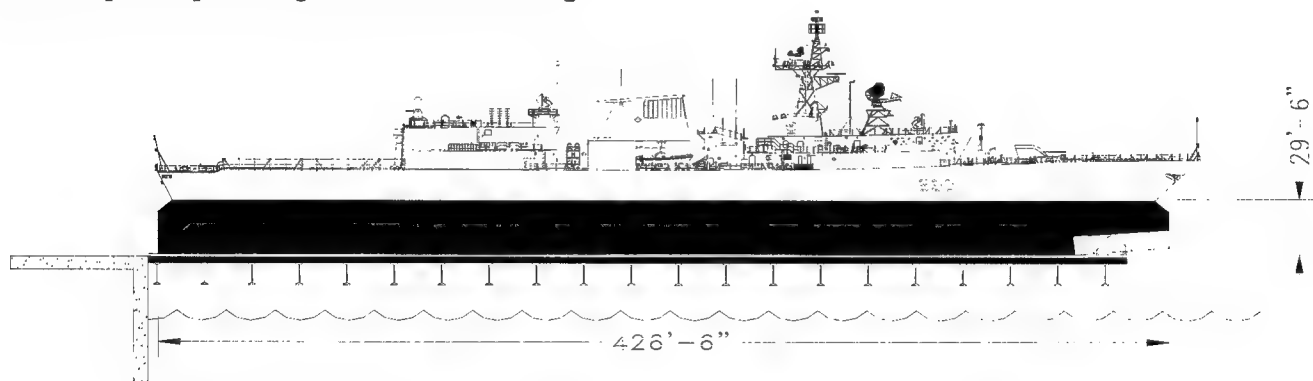
CHALLENGE

Our challenge is to protect the environment and conform to all the latest environmental regulations that have been legislated by all levels of government. Further to these regulations the Navy has also written guidelines that regulate the way we do our business with regards to the environment. Our fear as a ship repair facility was that the introduction of new environmental policies may put us out of business. This has not been the case as on average only three percent of the total cost of the refit has been spent on protecting the environment during the refit process. It is important to note that the emphasis has been from the beginning to prevent the discharge of effluents into the marine aquatic environment.

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REGULATIONS

FISHERIES ACT, RSC 1985c,F-14; Available on the Internet under URL,
http://canada.justice.gc.ca/ftp/en/laws/chap/f/f-14.txt
Maritime Command Orders, G-18, See ANNEX A Attached.

ENVIRONMENTAL IMPACT

During refits, our naval vessels are raised out of the water using a syncrolift. Increased environmental regulations were introduced into the work environment that had a direct impact on how we were to conduct our business during the refits. It was clear that an effective plan was going to have to be developed and a design conceived that would allow us to stay an industry leader and to protect the environment.

EVOLUTION OF A PROCESS

In the beginning the only requirement was to contain grit blast media in the form of aluminum oxide and the by-products that included lead based paint, antifouling, tributyltin, etc. This containment process was complicated by the fact that our work area was directly above the water on a syncrolift that extends four hundred and fifty feet out over the water. This process evolved into the complete capture of all liquids that were generated from the hydro blasting process that amounted to thousands of gallons. Further development of the process was to include capture of all particles generated from blasting and sanding of all areas above the waterline. The original systems consisted of loosely suspended tarps that were supported by sparsely spaced scaffolding and somewhat attached to the ships hull. The enclosure system has now evolved onto a rigid structure that has stood gale force winds in excess of seventy miles per hour without damage. This has been achieved by using an elaborate scaffolding and tarp system that is self-supporting in that no pressure is asserted on the hull in a high wind situation.

DESIGN AND CONSTRUCTION

The design and construction of the enclosure and capture system was developed in accordance with all applicable codes and regulations that include the Fisheries Act, Fire and Safety regulations, National Building and Electrical codes, Federal and Base environmental regulations and site authority inspections on quality. Specifications were developed that detailed the requirements of the work and the steps to be followed during construction. The purpose of the enclosure and capture system is twofold; one, to maintain sufficient temperature in winter and two, to allow for the capture of all liquids and particles generated during the refit. A comprehensive list of applicable materials had to be researched prior to writing the specifications. Sufficient latitude was given that, in consultation with the contractor new innovations could be explored. The specifications were written in a manner that would make the applicable contractor responsible for the end result. Attached is a specification that was developed to enclose HMCS Charlottetown that was dry-docked during the months of June through July 1999; See ANNEX B Attached.

WEATHER

Our Facility is located in eastern Canada in the province of Nova Scotia. The weather conditions in summer are quite pleasant with prevailing winds that are light and, usually from the southeast. In winter, conditions can change rapidly with high winds and temperatures well below freezing. These low temperatures can pose problems in dealing with liquids that freeze at thirty-two degrees Fahrenheit. It is common to have wind in access of seventy-five miles per hour accompanied by rain or snow. The design phase had to take into consideration that high wind would impact on the enclosure and that low temperatures would necessitate the need for heat. Weather conditions played a major part in selecting materials that would make the structure sound.

COST EFFECTIVE

During the initial development of the environmental process we have designed and implemented, there were concerns that the process would put us out of business. We have since come to learn that this is not the case. In fact the environmental portions of the last two major refits that we have done amounted to only three percent of the total budget to build a containment system. We have also had situations where we utilized the same capture system on more then one occasion thus further reducing our cost. Shown on page three is a chart that shows the percentage associated with protecting the environment in relation to the cost of the total refit of the vessel.

3%   15%

82%   **Capture System**
▓ **Enclosure**
■ **Repairs to Ship**
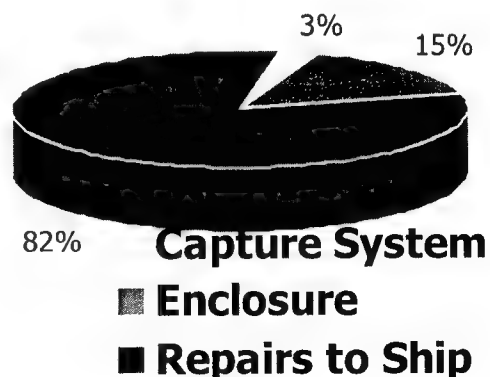
ANNEX A

Listed below are the Naval orders that govern how we are to conduct business in relation to protecting the environment.

MARITIME COMMAND ORDERS
SHIPBOARD ENVIRONMENTAL MANAGEMENT

PART I - GENERAL POLICY AND DIRECTIVES

References:
A. MARCORD 4-12 Maritime Command Environmental Program
B. CF and DND Policy on the Environment P5/92
C. CFAO 4-13 Reporting of significant incidents
D. CFTO C-81-011-000/MG-001- Operating and Maintenance Instructions - Oil tank and Bilge Cleaning Chemicals
E. C-03-005-033/AA-000 Naval Engineering Manual, Vol 1
F. MARCORD 66-5 Hazardous Material Management Program
G. MARCORD 66-9 Radioactive Material

Aim

1. This MARCORD provides guidance to ships on environmental management of shipboard waste.

Background

2. This MARCORD supersedes all pollution control management directives previously generated by MARCOM and it is complementary to the policy at reference A.

Scope

3. This MARCORD contains direction on environmental management of all waste for ships at sea and in harbour. The guidance provided herein reflects national and international regulations and conventions. The MARCORD is divided into three parts and the following areas of environmental management are addressed:

   a. Part I: General Policy & Direction;

   b. Part II: Waste Management; and

   c. Part III: Fueling.

General Policy

4. As directed at reference B, MARCOM will demonstrate responsiveness to and responsibility for protecting the environment in the conduct of all activities; and will adopt a sound environmental ethic, ensuring responsible partnership in the Government's overall environmental program. Specifically, it is CF, DND and MARCOM policy that the letter and spirit of all applicable federal environmental laws shall be met or exceeded and, whenever possible, compatibility with provincial and international standards shall be ensured. The MARCOM environmental policy is to be reflected in all pan-naval activities and operations. This MARCORD shall be fully adhered to except:

   a. when national security is threatened or when operating under the National Emergency Act; and

   b. for the purpose of saving life or preventing the immediate loss of a ship.

5. Annex A provides an overview of applicable pollution regulations. The *Canadian Environmental Protection Act (CEPA)*, the *Canada Shipping Act (CSA)* and the International Convention for the Prevention of Pollution from ships at Sea (MARPOL 73/78) were used in the development of this MARCORD. Annex B is a glossary to assist in the interpretation of various terms used throughout this MARCORD.

6. Commanding Officers (COs) shall take all reasonable measures to ensure their vessels comply fully with local harbour pollution regulations, unless specifically exempted by local port authorities.

NOTE: 1. As the principal pollution related tenets of the *Fisheries Act* parallel those of the *Canada Shipping Act (CSA)*, for simplicity, the definitions contained within the *CSA* are considered representative of both for the purposes of this MARCORD.

2. Any Unit, which is unable to comply with this policy because of equipment deficiencies or limitations, or any other factors, shall report the circumstances in writing through the chain of command.

PART II - WASTE MANAGEMENT

Liquid Waste

7. For the purpose of this order, the liquid wastes generated by ships are of the following types:
   a.   oily waste water;

   b.   black water;

   c.   grey water; and

   d.   ballast water.

Oily Waste Water

8. The oil pollution prevention requirements of this MARCORD are based upon provisions of the *CSA's* Oil Pollution Prevention Regulations which came into effect in 1993 and parallel Annex I of MARPOL 73/78. Oily waste water shall only be discharged overboard after treatment with oil separating or oil filtering equipment, and only under the following conditions:

   a.   if the post filtering and/or treatment oil content is:

        (1)   less than 5 parts per million (ppm) in inland waters; and

        (2)   less than 15 ppm outside inland waters; and

   b.   until 6 Jul 98, ships put in service (see Annex B) before 6 July 93 are permitted to discharge oily mixtures with an oil content up to 100 ppm, but only beyond 12 nm of any coastline (excepting in MARPOL special areas).

9. Equipment. The following equipment is deemed to meet the levels mentioned in paragraph 8 of part II:

   a.   only those oily water separators fitted with an oil content monitor (OCM) and recirculation line that prevent effluent exceeding 5 ppm from being discharged overboard shall be deemed capable of meeting the 5 ppm oil discharge levels; and

   b.   only those oily water separators fitted with an OCM and recirculation line that ensure oil discharge remains below 15 ppm is deemed to be oil filtering equipment that meets the 15 ppm oil discharge levels.

10. Ships not fitted with oily water separators or with inoperable OCMs, shall post a sentry to ensure discharge from the OCM remains clear and free of visible contamination (i.e. oil sheen visible in effluent with >15 ppm oil content).

11. Ships planning to visit/transit Arctic waters or MARPOL Special Areas (defined in Annex B) should contact their respective Formation Environmental staff for specific guidance.

12. Ships not equipped to meet the above effluent discharge levels, shall, within ship safety considerations, retain this oily waste water on board until it can be discharged to an appropriate reception facility.

13. Bilge Water. Ships' COs shall:

   a.   ensure that discharge to the bilge and bilge water levels are actively controlled to decrease the volume of oily waste water requiring processing;

   b.   prohibit discharge of machinery space oily waste water through an oily water separator in excess of the prescribed limits outlined in Part II, Paragraph 8; and

   c.   prohibit use of the oily water separator unless the ship is underway and outside of environmentally sensitive areas which include the following:

        (1)   MARPOL Special Areas;

        (2)   Australian Great Barrier Reef; and

        (3)   Arctic Ocean.

   d.   be personally responsible for authorizing the pumping of machinery space bilges directly overboard, i.e. not through an oily water separator.

   e.   ensure that chemical cleaning agents for cleaning tanks and bilges are used **only** when conditions permit transfer to a sullage barge or other facility designed for their acceptance. (Fluids containing such agents are considered to be contaminated. As such, they shall not be pumped overboard under normal circumstances. References D and E provide further direction on approved cleaning agents.)

Black Water

14. Present Canadian marine pollution prevention regulations only prohibit the discharge of black water in the Great Lakes. To comply with international standards, this section is also based on the provisions of MARPOL 73/78, Annex IV. Black water discharge regulations are outlined in the table at Annex A.

15. At Sea. Ships fitted with black water collection and/or treatment systems shall comply with the following regulations pertaining to black water discharge:

    a.   within 4nm of any coastline discharge permitted from treatment systems only;

    b.   between 4-12nm (Canadian Waters): discharge of untreated black water permitted, subject to the provisions of paragraph 18;

    c.   between 4-12nm (Other coastlines): discharge permitted from treatment systems; and

    d.   beyond 12nm of any coastline, ships are permitted to discharge all untreated black water overboard, subject to the provisions of paragraph 18.

16. In Harbour. Ships shall comply with local port regulations. Ships fitted with blackwater collection systems and/or treatment systems shall:

    a.   collect and discharge their untreated black water directly to a port facility if such facilities are available and their use is cost effective;

    b.   if permitted by local port authorities, discharge black water directly overboard. Such discharge should not be instantaneous but be done at a moderate rate, using the fitted discharge system;

    c.   collect black water for discharge at sea in accordance with paragraph 18, if the holding capacity so permits.

17. Due to the high cost of operation and maintenance associated with blackwater treatment systems, ships shall normally limit the operation of such systems to the following circumstances:

    a.   when harbour authorities prohibit the discharge of untreated black water, and reception facilities are not available;

    b.   when within regulated areas as outlined in paragraph 15 for periods which exceed the holding capacity of the vessel; and

NOTE: Operation of black water treatment systems is not necessary beyond 12nm of any coastline, except in special areas.

    c.   when in home port, vessels shall not normally operate their treatment systems. The exception to this is vessels fitted with biological treatment systems, which are designed to run on a continuous basis.

18. When at sea, black water that has been stored in holding tanks shall be discharged at a moderate rate while the ship is underway and proceeding at a speed of 4 knots or greater. It shall not be discharged less than the limits outlined in Annex A.

Grey Water

19. The environmental impact of grey water is minimal, provided no hazardous waste or chemicals have been mixed with it. Grey water is not presently regulated by the Canada Shipping Act or by MARPOL 73/78; however, a growing number of port authorities worldwide do regulate its discharge.

20. Grey water containing hazardous waste shall not be discharged overboard. To reduce the volume/limit the impact of grey water discharge, ships shall:

    a.   use soaps, detergents and cleaning agents supplied by the CFSS or their equivalent; and

    b.   limit the overboard discharge of fire fighting foam to that amount required to prove proper system functioning during trials or drills. Fire fighting foam shall not be discharged within harbour limits except in case of emergency or where specifically authorized by the appropriate HQ.

    c.   cleaning products, including soaps and detergents, are to be CFSS approved and/or equivalent or must be subjected to the review process outlined in paragraph 39(h).

Ballast Water

21. Due to the potential for the unwanted introduction of aquatic organisms and pathogens into foreign ecosystems, the following guidelines must be followed:

    a.   when ballasting and deballasting must occur, they are to take place outside of territorial waters in water greater than 200m in depth;

    b.   where ballasting/deballasting is necessary outside of the restrictions given in Paragraph 21(a), notification is to be provided to the Formation as soon as practical. The Formation will provide ballast disposal or pumping disposal instructions.

Solid Wastes

22. Categories. Under the provisions of MARPOL 73/78, the solid waste generated by ships is separated into the following categories:

a.   plastics, such as synthetic ropes, styrofoam, and plastic garbage bags;

b.   garbage, such as floating dunnage, lining and packing materials, paper, rags, glass, metals, bottles, crockery, and similar refuse; and

c.   food waste.

23. Disposal. Guidelines for the disposal of solid waste at sea are as follows:

a.   plastics shall not be disposed of at sea;

b.   non-pulped garbage shall not be disposed of at sea within 200nm of Canadian coastlines, anywhere in MARPOL special areas or within 25nm of other coasts. Where practical all non-pulped garbage should be retained on board for disposal ashore. If garbage is disposed of outside regulated limits, it should be made negatively buoyant prior to disposal. Plastic bags are not to be used for disposal;

c.   pulped garbage shall not be disposed of within 3nm of coastlines or anywhere in MARPOL special areas;

d.   pulped food waste shall not be disposed of within 3nm of coastlines, or within 12nm when in MARPOL special areas (unless operational requirements dictate otherwise); and

e.   non-pulped food waste may not be disposed of within 12nm of coastlines, including MARPOL special areas.

24. Recycling. Recycling is an integral component of an effective solid waste management program and contributes to the sustainability of our natural resources. All ships are fully encouraged to practice the 3 Rs of waste reduction (Reduce, Reuse, and Recycle) on board and to make maximum use of recycling programs and facilities where available.

Biohazardous Infectious Wastes

25. Biohazardous Infectious Waste (BIW) includes both medical and dental waste. While it represents a small proportion of a ship's total volumetric waste generation, it requires proper handling and disposal because of environmental, aesthetic and occupational concerns and its potential hazard to human health.

26. This section outlines procedures for the storage and disposal of BIW.

27. While any item that has had contact with blood, exudation or secretions may pose a hazard, it is usually considered impractical or unnecessary to treat all such waste as BIW. Thus the following items should be considered solid waste and not BIW: sponges, surgery drapes, lavage tubes, casts, disposable pads, disposable gloves, specimen containers, lab coats and aprons, and dialysis waste such as tubing, filters, towels and disposable sheets.

28. The ship's senior medical authority shall determine what constitutes BIW. The ship's CO is the approving authority for its storage and disposal.

29. BIW Holding Bags. Plastic bags used for this waste must be durable, puncture resistant, and able to withstand autoclaving. They shall be colour coded in accordance with the table below. All BIW shall be autoclaved and double bagged prior to storage and subsequent disposal.

30. Colour Coding for BIW Containers:

WASTE TYPE	COLOUR-CODING
Human Anatomical	Red
Microbiology Laboratory Waste	Yellow
Human Blood and Body Fluid Waste	Yellow
Waste Sharps	Yellow

NOTE: Ships shall acquire the proper BIW bags and containers from the CFSS.

Storage

31. BIW shall be stored in accordance with the following directives:

a.   storage areas must be totally enclosed and separated from supply rooms or food preparation areas;

b.   the storage areas must be secure to prevent unauthorized entry;

c.   the WHMIS biohazard symbol shall be prominently displayed on all containers designated for BIW;

d.   no materials other than waste are to be placed in the same storage area as BIW; and

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e.   whenever possible, BIW should be refrigerated at 4°C until final disposal.

32. Waste sharps shall be collected in plastic autoclavable sharps containers. To prevent accidental puncture wounds sharps should not be recapped, clipped, cut, bent or otherwise mutilated. All sharps shall be steam sterilized and retained on board for proper disposal ashore.

Disposal

33. All BIW aboard ships must be decontaminated by autoclaving prior to its final disposal. The overboard discharge of BIW is prohibited except under the provisions of paragraph 4 of Part I of this MARCORD. All dumping or discharge of BIW shall be the subject of a pollution incident message/report in accordance with reference C and directions from the appropriate Formation.

34. BIW must be disposed of in accordance with local disposal regulations. Such disposal will not be authorized except where appropriate local regulations apply and are in concert with the intent of Canadian environmental guidelines.

Hazardous Wastes

35. Hazardous Waste has the potential to adversely impact human health and the ecosystem in general. Every effort shall be made to prevent hazardous waste from entering other waste streams on board ship. Specific regulations governing the overall management of hazardous materials are contained in reference F.

Categories/Types

36. Hazardous material includes all dangerous substances, dangerous goods, hazardous commodities, hazardous products, and hazardous waste including, but not limited to, the following:

   a.   explosives;

   b.   gases;

   c.   flammable and combustible liquids;

   d.   flammable solids (i.e. those readily combustible on exposure to air, water, or water vapour);

   e.   oxidizing substances and organic peroxides (including chemox canisters);

   f.   poisonous and infectious substances;

   g.   radioactive materials;

   h.   corrosives; and

   i.   miscellaneous (e.g. asbestos, PCBs, and any hazardous waste not ascribable to other categories).

NOTE: Radioactive Material, PCB, and explosives on board ships are not covered in this MARCORD but   are covered in references F and G.

37. Hazardous waste shall not be dumped overboard except under the provisions of paragraph 4 of Part I of this MARCORD. Should it be necessary to dump hazardous waste, a pollution incident message/report shall be made to the appropriate Formation headquarters in accordance with reference C and Formation directions.

Return of Hazardous Materials

38. Current environmental legislation requires that hazardous materials be managed responsibly, ensuring the safety and well being of individuals and the environment. All ships are directly responsible for the proper care and handling of hazardous material from the moment it is delivered to its final acceptance by the supporting base or station as returned stores or waste. Essential elements of this management strategy include proper identification, labeling, and packaging prior to handling or transportation for return and disposal.

Handling of Hazardous Materials/Wastes

39. Many of the actions taken to ensure individual safety will contribute to environmental protection. The following factors shall be considered by all personnel who have a requirement to handle hazardous materials/wastes:

   a.   ensure that each container is **clearly WHMIS labeled** to identify contents;

   b.   ensure that the containers used are in good condition, are compatible with the material to be stored, have proper lids, caps, etc., and do not leak;

   c.   ensure that any containers temporarily stored outside without overhead cover are regularly inspected to guard against deterioration, loose lids, tops, etc., which could allow the contents to be released into the environment. These inspections should be logged. (Particular problems are created as the sun heats and expands the contents or as rain water enters containers causing overflows);

d. ensure that all pans or pails used to drain hazardous waste are completely emptied into appropriate containers. (Extra care must be exercised to ensure that drain pans are not left partially filled and exposed to rain which can cause an overflow);

e. to prevent spills, ensure that funnels are used when transferring liquids. (Frequent spills of small quantities quickly contaminate the environment and create unsafe working conditions);

f. regularly inspect all bulk containers for leaking valves, seeping bungs or caps. These inspections should be logged. Drip pans shall be utilized to catch small drips or spills;

g. ensure that all container storage areas are neat and organized such that containers will not be knocked over by personnel, wind or wave action;

h. ships are to ensure that new hazardous products are examined by a shipboard authority before they are allowed on board. This examination must include the possible non-hazardous alternatives, storage requirements and locations, and any special training requirements associated with the product;

i. hazardous materials are to be stored with due regard to compatibility. Hazardous Material General Storage Compatibility Charts are to be posted near HAZMAT storage areas to assist in identifying incompatible HAZMAT; and

j. take prompt steps to ensure the proper return and subsequent disposal of all hazardous waste.

k. Except in extreme circumstances, no hazardous waste shall be disposed of in foreign ports.

40. Although the directions above give details for the safe handling and storage of hazardous materials, as a general rule, all material should be handled in such a manner that personnel and equipment are not unduly exposed to any health or safety threat. In accordance with DND policy, WHMIS is applicable to all units. Reference F provides further guidance and direction regarding hazardous material policies and procedures for HMC Ships.

Air Emissions

41. MARCOM policies and guidelines governing air emissions during boiler soot blowing/smoke generation are contained in reference E. As a general rule, ships shall ensure that boilers, diesel engines, and gas turbines, are operated in such a manner as to minimize smoke emission.

Incineration

42. Hazardous material, including BIW, shall NOT be incinerated on board ships.

43. Every measure shall be taken to ensure correct and safe operation of shipboard incinerators. COs shall ensure that incinerators are properly fitted, maintained, and personnel are trained and take adequate personal safety precautions.

44. Incineration of combustible garbage may be used to reduce the volume of garbage that must be retained on board. Incinerators shall be operated as follows:

a. in general, any waste may be incinerated, with the exception of hazardous material and material which can be retained on board for recycling;

b. incineration residue (ash) shall be minimized through proper incinerator operation. Incinerators are to be "worked" to optimize their combustion efficiencies. Ash can be disposed of at sea beyond 12nm from the nearest coastline;

c. as an alternative, ash may be disposed of ashore. In this event, ash/remaining waste shall be thoroughly cooled, overhauled and securely bagged; and

d. Temporary incinerator operation is subject to the following additional restrictions:

(1) operation shall be specifically authorized by the ship's CO;

(2) such incinerators shall be correctly located on a ship's upper deck with adequate fire fighting equipment readily available;

(3) they shall be continually attended while in use; and

(4) they shall only be used during daylight hours and shall be controlled to minimize generation of smoke and visible flame.

PART III - FUELING

GENERAL

45. Every reasonable precaution shall be taken to prevent oil and hazardous substance spills, particularly during fueling or fuel transfer operations. Unnecessary discharges of oil and hazardous substances shall be avoided by developing correct operating procedures, and periodically checking for

proper functioning of equipment and systems.

46. Should a spill occur, the spread of the pollutant must be limited as soon as possible to reduce the potential for environmental damage. The necessary containment equipment shall be made available in the vicinity of potential incidents (e.g. on the jetty, near refueling sites, aboard ships, etc...)

47. Self-generated or observed pollution incidents at sea, in harbour or on land shall be reported in accordance with reference C and the directions from Formation HQs. MARCOM HQ N3, N4, N48 are to be informed of pollution incidents reported to the Formations.

48. Ships are required to use written fueling checklists in preparation for fueling. Completed checklists are to be retained on board for one year.

49. Following a spill, Formation Commanders may wish to consider ordering either an SI or TI in instances where such follow-on action is warranted.

Harbour

50. All MARCOM units and agencies shall make every effort to prevent, contain, and clean up oil and hazardous substance spills as directed in Formation orders.

51. Formations are to develop and promulgate ship class oil spill response plans which meet the intent of the *CSA*, as well as DND requirements. Ships are required to hold and keep current vessel-specific oil spill response plans based on the Formation supplied class plan.

52. To reduce the potential for, and impact of, an oil spill when fueling, the following procedures are to be effected:

    a. in Halifax and Esquimalt Harbours ships shall normally embark fuel, except JP5, during normal working hours;

    b. in Halifax and Esquimalt Harbours notice of intended fueling or de-fueling operations (including internal consolidation), shall be given in accordance with HCIs;

    c. when fueling or consolidation takes place in darkness, ships sides are to be illuminated and sentries placed to give warning of overflow; and

    d. a spill containment boom shall be placed around all vessels during fueling operations at DND berths. In submarines, the opportunity shall be taken to blow round while the boom remains in place.

Replenishment At Sea (RAS)

53. RAS operations are a potential source for oil pollution. It is estimated that a hose parting can release as much as 50 barrels of fuel even though pumps may be stopped and valves shut immediately.

54. RAS fueling operations will not normally be conducted within 12nm of a coast. Nevertheless, Ships' COs shall be cognizant of stricter restrictions on RAS by foreign coastal states (i.e. USN OPNAVINST 5090.1A - prohibits fueling operations within 50nm of a coast). All reasonable preventive measures shall be taken to minimize the potential for spills during the entire RAS evolution.

Additional Requirements For Ships Equipped With Water Compensated Fueling System (WCFS)

55. WCFS effluent shall not be discharged unless operational requirements necessitate. It is prohibited to discharge WCFS effluent if it does not meet the prescribed oil discharge levels.

56. Ships fitted with WCFS are required to take special precautions to prevent fuel discharge during refueling operations:

    a. refueling at sea shall not be conducted within 12nm of land; and

    b. in harbour, special arrangements shall be made to capture WCFS effluent and treat it as oily water. WCFS should not be released directly into the harbour; and

    c. when WCFS ships are fueled, the discharged water shall be routed through a sullage barge, and/or a jetty treatment system where available.

ANNEX B

ENCLOSURE SYSTEM

1. The purpose of this Environmental Enclosure and Floor system is to ensure that no effluent or particles from the hydro blasting process escape into the harbour.

2. FMFCS has a requirement to construct a hull enclosure system for the HMCS Charlottetown. The approximate start date for this project will be May 9 and will extend to July 7.

3. The contractor must supply all labour and materials necessary to erect, dismantle, maintain and remove this enclosure system from the site.

4. The contractor is responsible for performing required maintenance on the enclosure within four (4) hours after being notified by the DND representative.

5. A mandatory site visit by the contractor is required prior to award of contract.

6. OPI is D. Randall, Phone #902 427-0550-2663.

STATEMENT OF REQUIREMENTS

Structure

1. The HMCS Charlottetown will be located on the Syncrolift platform at the Halifax Dockyard.
2. The Contractor is required to construct a temporary self-supporting structure around the perimeter of the hull.

3. The approximate dimensions of the Charlottetown enclosure are four hundred and twenty seven feet (427') long, extending post the syncrolift, by sixty-two feet (62') wide.
4. The contractor is to construct one (1) enclosure within the main enclosure approximately thirty two feet (32') by forty nine feet (49') as indicated on this drawing. Exact location to be indicated on site.

5. This structure must allow for a minimum working clearance of six feet (6') from the hull at a minimum height that extends to two feet (2') above the Boot Top (approximately 29 feet (29') above the syncrolift).
6. The structure must allow for:

a) one (1) brow stand at the stern,
b) one (1) large equipment access door at a size of twelve feet (12') high and eighteen feet (18') wide also located at the stern of the ship,

c) one equipment/personnel door at a size of six feet (6') wide and eight feet (8') high located at the stern on the port side, ten feet (10') from corner as indicated on drawing.

d) and two (2) additional personnel access doors of no less than three feet (3') wide and six feet eight inches (6'8") high as indicated on drawing.

These doors listed above must be rigid and fully retractable with a watertight seal.

Final locations for oil doors and brow stand are to be determined by site authority. Approximate locations are shown on drawing.

Enclosure

1. The enclosure must be capable of withstanding adverse weather conditions in the Halifax Harbour vicinity.

2. The enclosure shall be affixed to the hull to provide a weather tight seal without allowing the structure to exert force on the hull.

3. Ships blocking is to be made watertight using 8 MIL polyethylene.

4. The enclosure must be weather tight to allow inside temperature to be maintained by DND.

5. The material used to create the enclosure shall be translucent such that a sufficient amount of light will pass through to allow for work operations in the enclosure.

Floor Surface

1. The contractor shall supply/install and remove five eighths inch (5/8") G&T spruce standard (4' X 8') sheets of plywood to the deck of the syncrolift in a manner to eliminate cold and drafts from entering the enclosure. Joints in the plywood are to be sealed to make them watertight.

2. The contractor is to install a watertight curb around the perimeter of the plywood floor using four-inch (4") X four inch (4") spruce timber. This timber is to be sealed tight to the plywood as indicated in Typical Curb Detail shown on this drawing.

CONCLUSIONS

The Department of National Defense, Fleet Maintenance Facility on Cape Scott, in Halifax, NS has shown that it is possible to conduct large-scale complete refits and keep ourselves in business while protecting the environment. We have conducted five large-scale refits using the process that I have designed with complete success. We have also demonstrated repeatability with the capture system and utilized it through six cycles on the syncrolift. This has served to reduce our operating costs when docking a ship thus, reducing the cost of the overall refit. I will continue to work on improving methods that will be more productive as the evolution of the process continues. It is important to note that all of the materials that were used in the design of the capture system have been sold to recyclers. It is important to note, that since we have used these capture systems on a large scale, we have not had one instance where we have had an environmental spill into the harbour.

Development, Demonstration and Validation of Zero Discharge Industrial Waste Water Treatment Plant (IWTP) At Puget Sound Naval Shipyard (PSNS), Bremerton, WA

Katherine Ford, NFESC, Walter Hunter, PSNS,
Ronald Bruening, IBC Advanced Technologies,
Todd Lloyd, Pro-Spec Engineering, Greg Levcun, NUWC Keyport,
Linda Weavers, Ohio State University, and
Hugo Destaillats, California Institute of Technology

ABSTRACT

In FY94, the Office of Naval Research (ONR) tasked Naval Facilities Engineering Service Center (NFESC) to investigate emerging technologies for design of a zero discharge industrial wastewater treatment plant (IWTP) process. This IWTP RDT&E effort will enable Navy shipyards to treat wastewaters to the regulatory levels expected from the reauthorization of the Clean Water Act. The major influent Navy industrial wastestream to the IWTP is from shipyard metal finishing facilities. At PSNS, 90% of the wastewater volume is from (1) acid/alkali cleaning wastewaters, (2) chromium plating rinsewaters and (3) cyanide process wastewaters. Hydroxide precipitation is the conventional method for removal of heavy metals from these three wastestreams with the generation of hazardous sludge that must be sent to a landfill. Cyanide oxidation is by sodium or calcium hypochlorite prior to bulk precipitation. In addition to elimination of the sludge producing metals precipitation process, management of total toxic organics (TTO's) and biological vector control has to be considered. This paper will discuss the combinations of chemical, sorption/desorption, membrane processes, and advanced oxidation processes (AOP) that have been evaluated as modular components for designing a zero discharge IWTP, or to minimize point source discharges as found in Navy dry dock operations. Many of these innovative wastewater treatment technologies are capable of dual use on shipboard at sea or while homeported. In FY94, and economic cost analysis was performed for potential treatment technologies for design of a zero discharge IWTP (Little, A.D., 1995).

Keywords: molecular recognition technology, zero discharge industrial wastewater treatment plant, hexavalent chromium, electrowinning, advanced oxidation processes, total toxic organics, anionic and nonionic surfactants, advanced reverse osmosis, ultrasonics, and sonolysis

INTRODUCTION

For the Navy as well as other DoD agencies, generation of these large volumes of industrial processing sludge will be restricted by Executive Order 12856 as stated in the Federal Compliance with Right to Know Laws and Pollution Prevention Requirements. In the next century, "the Federal Government should voluntarily set goals to reduce their agency's total releases of toxic chemicals to the environment and off-site transfers of such toxic chemicals by 50 percent by December 31, 1999, to the maximum extent practicable through source reduction". Heavy metal removal technology must enable DoD facilities to treat to the levels expected from the re-authorization of the Clean Water Act (CWA). Under CWA, DoD agencies will be required to meet the National Pollutant Discharge Elimination System (NPDES) and the General and Categorical Pretreatment Standards

under Section 307(b) and 307(c) of the CWA. The ultimate goal of a zero discharge IWTP design is to recycle effluents and eliminate the generation of hazardous sludges. This zero discharge IWTP RDT&E program has been undertaken in five separate efforts: 1) metal recovery/recycle acid/ alkali wastewaters, 2) recycle Cr (VI) from rinsewaters to process plating bath, 3) cyanide oxidation, and 4) destruction of total toxic organics. Surfactant destruction/deforming has been added since the ONR's inception of the zero discharge IWTP concept. Surfactants are increasing in volume in industrial wastewaters due to the change in parts cleaning processing from organic solvents, such as trichloroethylene (TEC) to alkaline cleaners. Lastly, metal monitoring technologies have been sought for IWTP processing operations. The use of an automated trace metal analyzer (ATMA) during testing of the MRT acid/alkali system will discussed by Mike Putnam of SPAWARS SYS CEN, San Diego in these Proceedings.

Puget Sound Naval Shipyard's IWTP was chosen for pilot scale demonstration due to its large industrial operations which include several metal plating and cleaning operations, such etching, passivating, plating, galvanizing and general cleaning. These processes generate rinse waters that must be treated by the IWTP before being discharged to the POTW, Bremerton, WA. The Shipyard (proper) encompasses 179 acres of land, 130 buildings, and seven permanent piers of deep water space. The shipyard has six dry docks, one of which is the largest in the U.S. Navy. The Naval Underwater Warfare Center (NUWC), Keyport, WA has also been selected to demonstrate advanced membrane technologies for cyanide process wastewaters. NUWC Keyport is involved in the first field studies for treatment of surfactant laden IWTP wastewaters. There is continuing coordination between PSNS and NUWC for exchanging information regarding emerging wastewater treatment technologies.

I. HEAVY METALS RECOVERY/ RECYCLE WITH SORPTION/ DESORPTION TECHNOLOGIES

Alternative methods to reduce sludge generation have been sought by changing the chemistry of the precipitation process. Sodium sulfide/ferrous sulfate (SS/FS) is a process for the reduction of hexavalent chromium (Cr VI) to trivalent chromium (Cr III), and precipitation of heavy metals such as cadmium, copper, lead, nickel, and zinc from industrial wastewaters. The SS/FS process results in a reduction in the quantity of sludge generated by 20 to 30% and has in an annual cost saving of $35,000 at NUWC Keyport (Durlak, 1997).

However, to avoid hazardous sludge altogether, a primary requirement of an alternative technology is that it be capable of removal of heavy metals ions such that they are selectively segregated from the wastestream in order to *recycle* to a process or *sell* to a reclaimer. An additional requirement is that the technology must remove the chromium below the current discharge standards in the *presence of other dissolved solids*. Besides heavy metal contamination, wastewaters often contain large concentrations of alkali metals (Na, K) and alkaline earth metals (Be, Mg, Ca,) which are not regulated. These metals do not need to be removed from the water before recycling, as would occur with conventional ion exchange technology.

NFESC investigated and reported the bench scale results of three novel metal adsorption technologies for sequential and selective heavy metal recovery in FY96 (Ford, K., 1996). In FY98, IBC Advanced Technologies was selected for pilot plant scale-up optimization studies leading to full-scale pilot demonstration at PSNS IWTP. IBC's ligand based adsorbent, patented as Superligs©, is a highly selective, non-ion-exchange process using organic ligands that are chemically bonded to solid supports such as silica gel (Bruening, R.I., 1991, Izatt, R.M., 1990). The metal selectivity is

achieved on carefully engineering the size and shape of the ligands (i.e., cavity dimensions, geometry, donor atom placement and type, and ring number and substituents as shown in Figure 1). Hence, the name for this technology is molecular recognition technology (MRT). Figure 1. illustrates one of these cavity-like, cyclic polyethers (crown ethers) that captures the metal ion, such as copper (Cu).

In Figure 2, the *sequential* removal process is illustrated using IBC's patented macrocyclic ligands. This scheme shows the separation and elution conditions for Ag, Cu, Cr (III), and Cd by four columns from a representative Navy acid/alkali wastesteam.

In FY98, the Environmental Security Technology Certification Program (ESTCP) funded a pilot scale demonstration at PSNS IWTP. Although the original intent of the ONR R&D was for sequential and selective removal of heavy metals for direct recycle, column design can be changed to meet Navy requirements. For example, Figure 3 shows that a MRT column can be designed for removal of only copper in the influent feed stream. Potentially this single metal removal design could be used for Navy ships dry dock operations where discharge limits are very stringent for copper.

Figure 1. Schematic Showing Macrocycle Ligand, Spacer, and Solid Polymeric Base

SEPARATION SCHEME FOR NAVY ACID/ALKALI WASTESTREAM
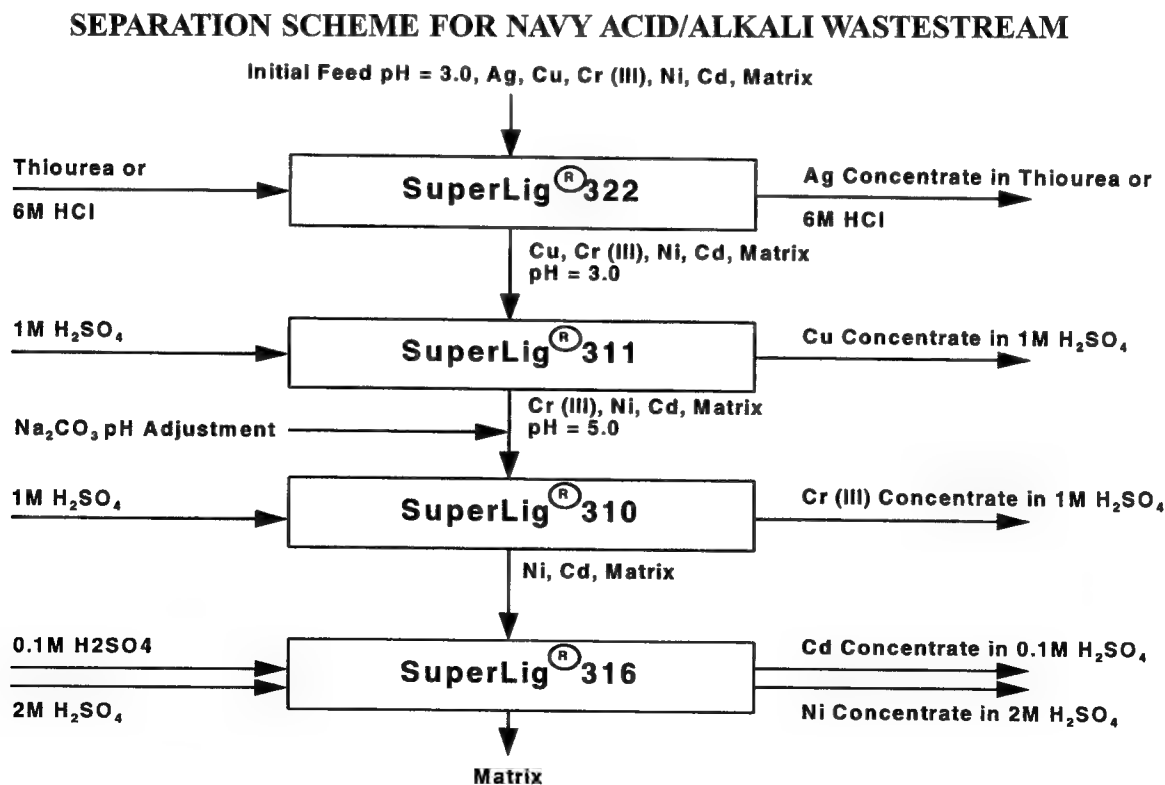
Figure 2. Column Separation Scheme for Removal and Concomitant Individual Separation of Ag, Cu, Cr (III), Ni, and Cd from Navy Acid/Alkali Wastewater

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MRT Selective Removal of Copper
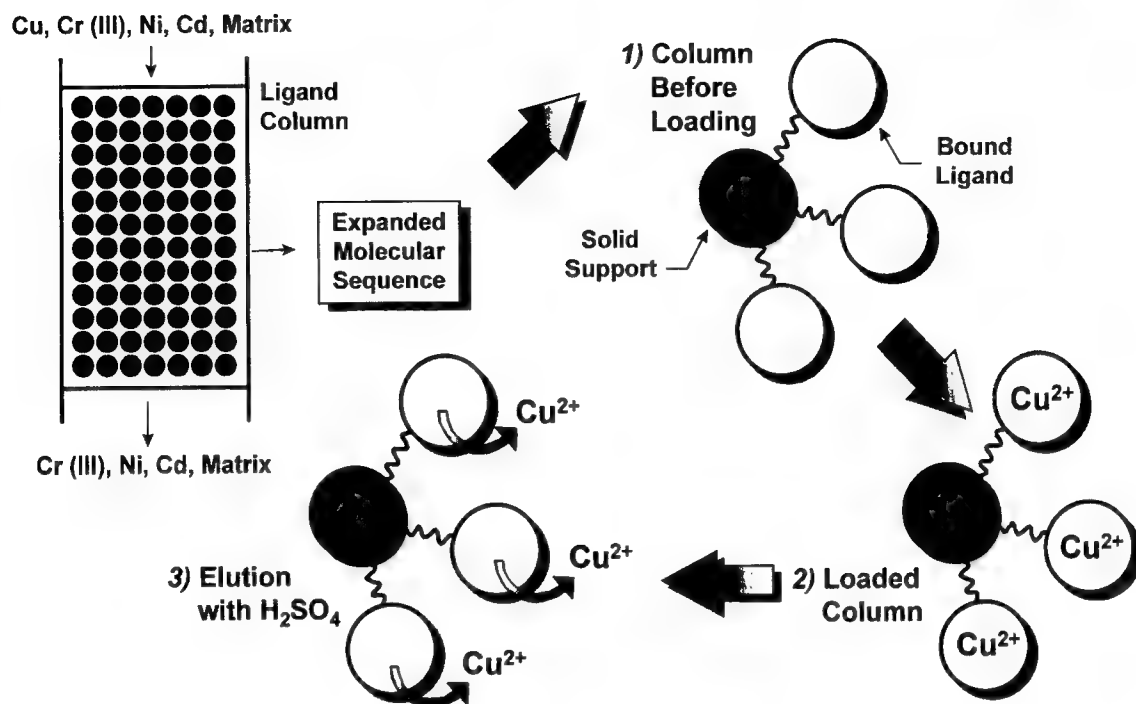
Figure 3.   MRT Column Selective Removal/Recovery of Copper Ion.

MRT Acid/Alkali System with Addition of Chromium MRT System
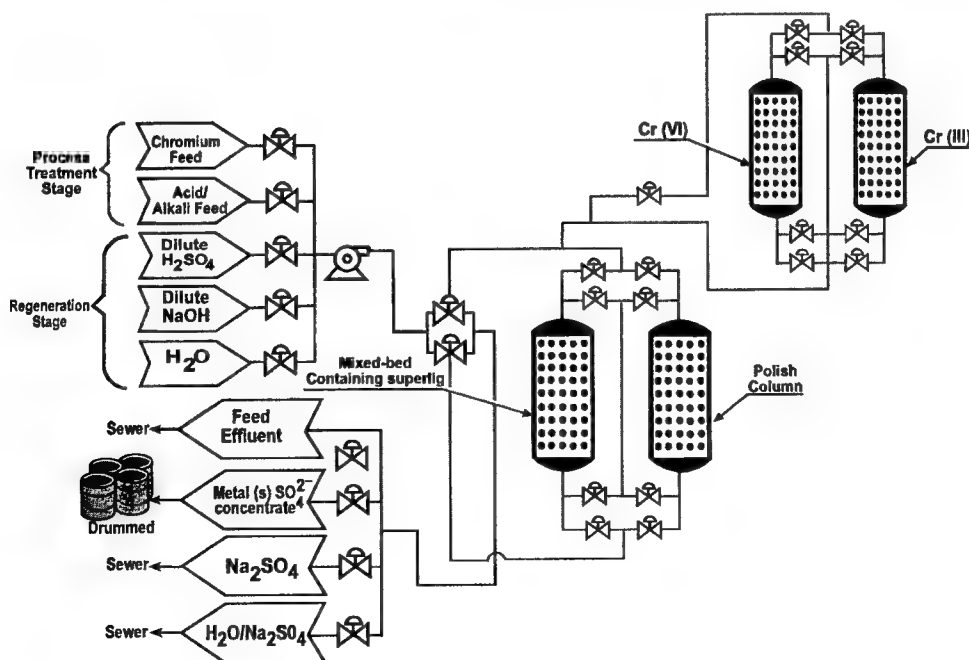
Figure 4.   Schematic of PSNS Industrial Wastewater MRT System

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Metal	Influent mg/l	Effluent Mg/l	Discharge Limit Mg/l	% Extraction	Affinity Constnat
			mg/l		
Mg	18.1	17.6	NA	2.5	0.02
Cd	0.7	0.005	0.17	99.4	13.8
Cr*	6.5	0.068	1.71	98.9	30
Cu	16.4	0.01	2.07	99.9	22
Ni	4.8	0.02	2.38	99.6	17
Pb	0.7	0.002	0.43	99.8	
Zn	9.4	0.099	1.48	98.9	14.4
Ag**	ND	NA	0.24	NA	13.8
Conditions: 1350 gals wastewater processed with flow rate 2 gal/min					
*Cr Discharge limits are for Total Chromium, Affinity Constant is for Cr (III)					
**Batch Did Not Contain Ag or Non-Detect					
*** Concentrations over 100% due to metals in sulfuric acid and PSNS water					

Table 1. **MRT Operation Test Run One (1) for Acid/Alkali Wastestream**

The industrial wastewater at PSNS IWTP contains only small quantities of precious metal silver. Therefore, a mixed Superlig bed column was favored over sequential and selective metal recovery as in Figure 2. Because chromium (VI) can be recycled back to the PSNS metal finishing facility, the wastewater will first be processed to remove Cr (VI) and Cr (III). See Figure 4. for the column design at PSNS's demonstration.

In FY99, the MRT system was installed for operational testing. . The preliminary results of this first operational testing are shown in Table 1. The analytical results show that magnesium (an alkaline earth metal) passed through the MRT column. The affinity constant being very low of 0.02. For all heavy metal the concentrations in the effluent stream were two orders of magnitude below PSNS monthly regulatory discharge limits for PSNS.

II. Chromium (VI) and (III) Treatment

MRT was equally successful in separating Cr (VI), Cr(III), Cu, and Ni into individual concentrates from a typical Navy chromium wastestream. It is significant to note that using MRT technology eliminates the conventional chemical reduction of Cr(VI) to Cr (III) prior to precipitation. During the acid/alkali MRT operational runs at PSNS, a Cr (VI) recovery system was not in place. The mixed bed column contained Superlig for Cr (III) recovery. Total chromium (Cr VI & III) for the pilot demonstration will be evaluated in FY00.

III. CyanideTreatment Using Advanced Reverse Osmosis and Electrowinning

Cyanide wastewaters are primarily associated with electroplating shops located within the shipyard. The Navy generates in an excess of 550,000

gallons of cyanide wastewater annually. It is anticipated that the volume of cyanide based plating will decrease as other non-cyanide based coatings are developed (EPA 1994). Several cyanide treatment technologies have been evaluated using ion exchange (Little, 1993), reverse osmosis (Zapp, 1993) and electrowinning (Ford, 1994 & 1995). However, due to the high "throwing power" of the cyanide plating baths, the Navy will continue to use silver and gold cyanide plating baths, particularly for nuclear work. The conventional treatment process for cyanide is to oxidize the cyanide wastesteam by alkaline chlorination. The cyanide is oxidized to cyanate, which is non-toxic.

An integrated advanced membrane treatment process for cyanide is shown in Figure 5.

This process consists of a combination of advanced reverse osmosis and electrowinning technology.

The cyanide wastewater is pumped to the advanced reverse osmosis (ARO) unit where the dissolved metal cyanides are concentrated prior to treatment by the electrolytic recovery unit (ERU). The permeate from the ARO is recycled back to the cyanide process. After positive results from field tests at Naval Air Station North Island metal finishing facility, a full scale demonstration is being tested at Naval Underwater Warfare Center, Keyport, WA. A report on the demonstration at Keyport will be released in FY00. Prior studies have shown higher ERU metal platting efficiency on a single metal rinsewater tanks (Ford 1994 & 1995) than that shown for bulk processing of 500 gallons at Keyport. There are on-going R&D

Cyanide: Advanced Reverse Osmosis Treatment System
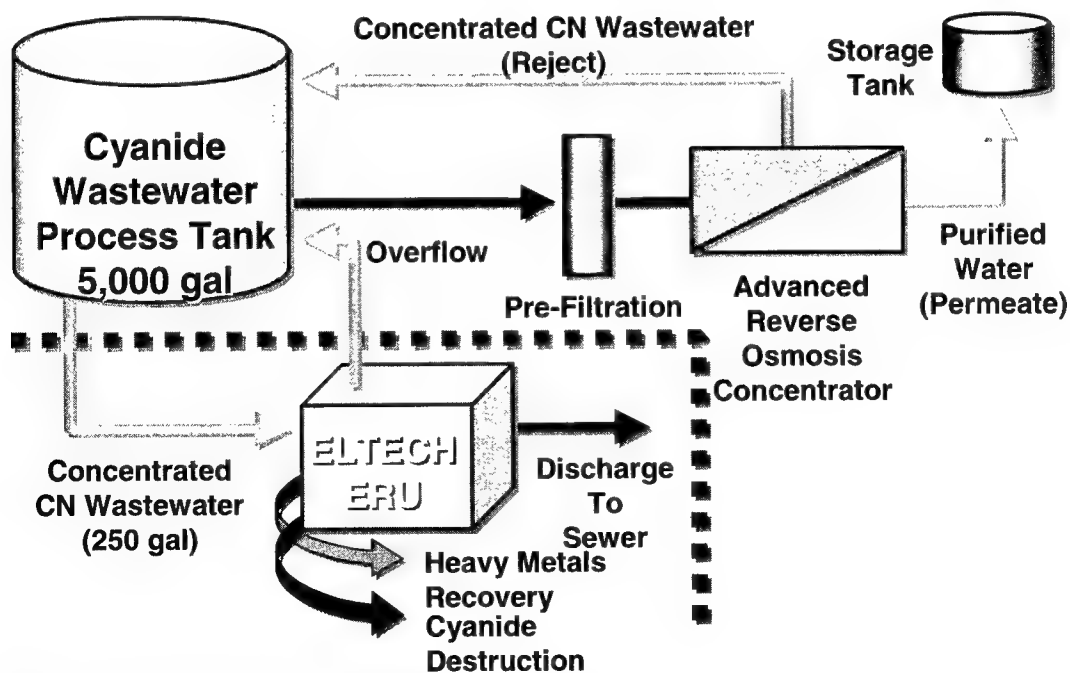
*Tom Kang, PI, NFESC, Code 421

Figure 5.   Cyanide Advanced Reverse Osmosis/Electrowinning Treatment System

efforts, supported by ONR and Strategic Environmental Research Development Program (SERDP), for improvement of ERU design for metals recovery at the cathode and oxidizing capability at the anode (Weres, 1999)

IV. Advanced Oxidation Process for Total Toxic Organics (TTOs)

Navy activities generate industrial wastewaters containing toxic organic contaminants such as phenols, methylene chloride, and tricloroethane from various plating shop cleaning and paint stripping operations. Over 3,680,000 tons of wastewaters containing TTOs are treated annually by IWTPs at Navy locations. These plants are not specifically designed for the destruction of organics. They cannot consistently meet Federal discharge limits for total toxic organics (TTOs) which is determined by sum total of the concentrations of specific organic contaminants whose individual concentrations exceed 0.01 ppm. Some activities have added carbon adsorption for organics removal, resulting in costs of over $10,000/month for disposal of the spent carbon. Effective and affordable treatment methods need to be developed for complete mineralization of toxic organics to meet existing requirements and the more stringent regulations that will be imposed by the impending amendment of the Clean Water Act.

It is possible to mineralize refractory organics down to very small levels using advanced oxidation processes (AOP) such as UV, UV/ peroxide, and UV/ozone. However, obstacles to the effective utilization of these UV systems are 1) the relatively inefficient use of the solar spectrum and 2) the light delivery to a photocatalyst can be impeded by UV absorbing components in the waste stream. For these reasons, evaluation of *second generation* AOP reactors is being investigated. The free hydroxyl radicals are generated directly from the water, i.e., *in situ*, to oxidize organic contaminates. Thus, the reaction does not require the use of chemical additions such as hydrogen peroxide. The equations below illustrate the differences between UV/peroxide and an emerging wastewater treatment technology such as sonolysis (ultrasonics).

Established AOP Treatment by Ultraviolet Irradiation

$$H_2O_2 + UV \rightarrow 2\ ^{\bullet}OH$$

$$\text{Organic Molecule} + {}^{\bullet}OH \rightarrow CO_2 + H_2O$$
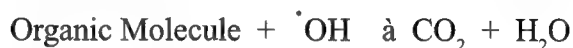
Emerging AOP *In-situ* Treatment by Ultrasonics

$$H_2O \rightarrow {}^{\bullet}H + {}^{\bullet}OH$$

$$\text{Organic Molecule} + {}^{\bullet}OH \rightarrow CO_2 + H_2O$$
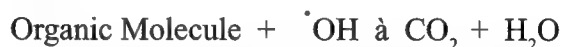
When ultrasonic-wave energy is transmitted in the water, destruction of organic compounds results from the formation of microbubbles. The microbubbles gradually grow with the ultrasonic frequency cycles until they attain a critical size, then collapse. As a result of this collapse, a large amount of energy and pressure is released. Water molecules under these conditions are decomposed to extremely reactive radicals. If organic compounds are present, they are directly destroyed. The final products of this process may be hydrogen, carbon dioxide, and/or some inorganic compounds (Suslick, 1989, Hoffmann, 1996, Hua, 1997, and Colussi, 1998). Over the last ten years, California Institute of Technology's Keck Laboratory has made significant advances in the application of ultrasonic irradiation to wastewater treatment. Model compounds, which mimic those found in Navy waste stream have been investigated (Kotronarou, 1991, 1992, and Hua, 1995, 1996) The effect of ozonolysis combined with sonolysis has also been extensively studied (Kang, 1998, Weavers, 1998). Recent investigation of the effects of frequency, temperature, hydrostatic pressure, and applied power have shown that optimization potential for the Navy's varied

requirements is possible. Keck Laboratory results indicate that high frequency ultrasound in the range of 400-600kHz is best suited for a wide range of wastewater applications. The induced chemical reaction rates have been found to be the highest in this frequency range. Another advantage of this frequency range is the absence of audible sound emissions. Since most readily available commercial sonication devices are limited to a frequency of 20 kHz, the equipment and facilities available in the Keck Laboratory for high fr4euqncy sonochemcial application are unique.

NFESC is testing a high frequency ultrasonic reactor system at Keck Laboratories for mineralizing methylene chloride and phenols from the influent wastesteam at Naval Air Station North Island, San Diego. In addition, wastewater samples from PSNS IWTP have been sent to Keck Laboratory for conformational studies. Keck Laboratory will perform detailed chemical analysis of the reaction intermediates and final reaction products generated during the ultrasonic irradiation experiments. The information is extremely important since it is essential to know if the target molecules are converted to other equally problematic products or if they are converted readily to innocuous products.

V. Treatment of Surfactant Laden Industrial Wastewaters

Many DoD activities are using aqueous immersion cleaning as a replacement for vapor degreasing solvents (Kodres, 1997). This usage is expected to increase with the restrictions on organic solvent cleaners, particularly those containing ozone depleting substances (ODS). UV irradiation treatment has been ineffective with these chelated metals due to the spectral interference of dissolved materials in the wastestream. At the Army's Lake City Army Ammunition Plant (LCAAP) the presence of chelated metals require increased polymer dosage prior to the bulk precipitation process. New surfactants and detergents are

created continuously to replace existing detergents and solvents in cleaning processes. These "improved" detergents are often more difficult to treat and result in fouling of wastewater treatment processes. For example, at the Naval Underwater Warfare Center in Keyport, WA, the use of a variety of non-ionic, and anionic surfactants results in failure of the chromium reduction and polymer flocculation processes. The EPA suggested solution of segregating waste streams before treatment does not work in this case because the chromium and surfactants are generated together. It is estimated that the lack of a treatment solution for this waste stream costs from $30,000 to $60,000 annually at Keyport alone. Other sites such as the Marine Corps Logistics Base in Barstow, CA have similar problems with surfactants. Therefore, methods to treat surfactants need to be developed.

A surfactant is a substance that adsorbs onto surfaces or interfaces and alters the interfacial free energy of the surface. Destruction of biodegradable surfactants typically occurs by biological treatment processes in wastewater treatment plants. However, biological treatment is often land intensive, expensive, and requires careful maintenance. Surfactant use is based on a variety of properties including foamability, chemical stability, solubility, reactivity, and corrosivity. For some applications it is not feasible to select a surfactant that is biodegradable, and it is possible that its toxicity properties are not well characterized or understood (Lewis, 1992). Ultrasonic irradiation of aqueous solutions has been shown to be effective for the *in situ* destruction of a variety of organic and inorganic contaminants (Francony and Pétrier, 1996; Hua and Hoffmann, 1996; Kontronarou, Mills et. al., 1991; Kontronarou, Mills et al., 1992; Pétrier, Micolle et al., 1992). Ultrasonic irradiation produces cavitation bubbles which yield internal bubble temperatures on the order of 5000 K and pressures of hundreds of atmospheres upon their implosion (Leighton, 1994). The interior of a

cavitation bubble contains water vapor, gas and volatile compounds. Destruction of organic compounds occur in the cavitation bubble itself or at the interfacial sheath by direct pyrolysis or hydroxylation which results from the gas-phase pyrolysis of H_2O: $H_2O \rightarrow H\bullet + OH\bullet$

In addition, polymers such as long-chained-polymeric surfactants are subject to destruction by pressure and shear forces generated as the bubble collapses. Reactions are also possible in the bulk aqueous phase by oxidation with hydrogen peroxide which is formed in sonolytic systems from the self reaction of $OH\bullet$, or the scavenging of $H\bullet$ by O_2 and the subsequent self reaction of $HO_2\bullet$. Sonication has been shown to be particularly effective with volatile and hydrophobic compounds since they can partition to the bubble or interfacial sheath rapidly. Surfactants are expected to exhibit similar reactivities due to their tendency to accumulate at the bubble interface.

Sonoluminescence, a weak emission of light, also results from an acoustically cavitating bubble when high intensity ultrasound propagates through a liquid. Although sonoluminescence was first reported in 1934, the exact mechanism of the emission is still under debate. Lasting for less than 50 picoseconds, the light emission occurs in the final stages of bubble collapse when the contents of the bubble are under extreme temperature and pressure. A recent study has explored the role of surfactants and surface active agents on the intensity of sonoluminescence (Ashokkumar, Hall et al., 1997). They determined that the relative sonoluminescence intensity increased in the presence of an anionic surfactant, sodium dodecylsulfate (SDS), or a cationic surfactant, dodecyltrimethlyammonium chloride (DTAC). Sonochemistry and sonoluminescence

are interrelated since violently collapsing bubbles generating high temperatures and pressures are required in both cases. Thus, increased sonoluminescence is expected to correlate with increased sonochemical activity. Also, the presence of a surfactant at a bubble surface has been shown to allow more rapid growth of a cavitation bubble by a process called rectified diffusion (Fyrillas and Szeri, 1995). This could result in a larger number of active cavitation bubbles and fewer bubbles that are growing to a radius where they will collapse violently. If bubbles are oscillating, but not cavitating, ultrasound is energetically inefficient. It is preferable to expend the ultrasonic energy to cause the cavitation bubbles to implode violently, and hence generate oxidizing free radicals.

The investigation at Ohio State University will determine the effectiveness of the sonochemical destruction of surfactants typically found in industrial wastewater treatment plants. For chemical experiments a near-field acoustical processor (NAP) with an ultrasonic irradiating area of approximately 1500 cm^2 will be used. The NAP will be temperature controlled by cooling the transducers. In addition, the reactor solution will be run in a continuous loop with a reservoir and pump in-line to monitor the ultrasonic reactions and reaction conditions as well as control the circulating flow rate. Real systems are very complex, therefore, it is often beneficial to investigate synthetic systems before the more complex matrix of a wastewater is explored. Ohio State University is currently studying the sonochemical reactions of a variety of nonionic, anionic, and cationic surfactants found in Keyport's influent wastewaters. These synthetic solutions will be based on realistic conditions in the industrial wastewater treatment plant.

GENERAL SUMMARY

Removal of trace heavy metals to well below detection limits, mineralization of refractory organics down to very low levels, and destruction of nonfilterable bacteria/viruses are possible in the dispersed/solution phase with a combination of state-of-art and newly emerging chemical processes. These processes would eliminate clarification problems, sludge drying and disposal, and variations in outflow quality. The effluent would meet industrial quality standards and be suitable for recycling.

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Contamination of Butyl- and Phenyltin Compounds in Sediment from Shipyards in Korea

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ABSTRACT

Butyl- and phenyltin compounds were quantitatively determined in surface sediments and sediment cores from near shipyards. Tributyltin (TBT) and triphenyltin (TPT) concentrations reached up to 46100 and 308 ng Sn/g on dry weight basis at the front of shipyard, respectively. Horizontal distribution of butyltin compounds was closely related with harbors and shipyards. Butyltin and phenyltin concentrations were relatively low where remote from the sources. Vertical distribution of organotins in sediment showed active use of them in Korean peninsula for past decades. The half-lives of organotins in a year scale provides a concern on persistence of these compounds in marine environment.

Keywords: Tributyltin, triphenyltin, shipyard, sediment, half-life

INTRODUCTION

Organotin compounds are among the most widely used organometallic chemicals. Production of organotins has increased for various purposes since their first biocidal application in the early 1920s (Thompson *et al.*, 1985). One of the major applications lies in heat stabilization for synthetic polymers and another lies in their use as agricultural biocide (WHO, 1980). Tributyltin (TBT) used as biocidal additive for antifouling paints has received much attention since its adverse effects on oyster farms near marina were revealed in the early 1980s (Alzieu, 1986). A series of studies have showed that TBT is highly toxic toward various non-target marine organisms (for review see Fent, 1996). Starting in the 1980s, many industrialized countries have regulated the use of TBT in antifouling paints. There is no regulation on application of TBT based antifouling to ship hulls and releasing of waste water

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containing TBT from shipyard in Korea yet. Furthermore, organotin contamination even in high potential area like shipyard has not been yet well documented.

Tributyltin is mainly introduced to marine environment through leaching from antifouling paint applied on ship hulls. Municipal wastewater may also partially account for input (Chau *et al.*, 1992). It is difficult to identify the sources and pathways of TBT with a limited monitoring study due to its complex behavior in marine environment. In most studies, the contamination of TBT has usually been monitored at only a few selected points (*e.g.* Tolosa *et al.*, 1992). The samplings were frequently concentrated near harbors, which has very little ecological significance. Extensive survey data of TBT covering a whole basin are seldom available. Limited sampling density has often made it difficult to evaluate how far TBT contamination has spread from the source areas.

Vertical distribution of chemicals in sediment cores provides the history of contamination. Not only the trend of organotin contaminant for past several decades but also half-lives of organotin can be inferred from the vertical distribution. The half-life of TBT in seawater was known to be from days to weeks, while that in sediment exceeded several months in laboratory study (Adelman *et al.*, 1990). The half-life of TBT estimated from the sediment core samples was longer than several years (de Mora *et al.*, 1989). However, the half-life of triphenyltin (TPT) has not been estimated with field samples. Although use of TBT was banned from the early 1980s, TBT has still been detected from the marine sediments (Quevauviller *et al.*, 1994). Desorption from the sediment associated organotin is regraded as one of possible TBT input sources. In ecotoxicological concern, trend of organotin contamination and their extent of persistency in the marine ecosystem are important.

In the present study, butyl- and phenyltin compounds in surface sediments and sediment cores were quantitatively determined to study horizontal and vertical distribution of these compounds. Surface sediments were more extensively studied in major shipyards in Korea to reveal sources and pathways of organotins. Organotins in sediment core were analyzed to investigate the trend of past organotin contamination in Korea and to estimate the half-lives of TBT and TPT in sediments.

MATERIALS AND METHODS

Study Area

Ten surface sediment samples were collected from Ulsan Bay in 1996, where two large harbors and a repairing shipyard is located (Fig. 1). Five sediment samples were collected from Okpo Bay in 1996, where one of largest shipyard in Korea is located (Fig. 2). Sediment cores were also taken from St. 5 in Ulsan and St. 3 in Okpo Bay in 1998.

Sample Collection

Surface sediment samples were collected, using a van Veen grab. Approximately the top 2 cm of sediments were taken by a stainless steel spoon and stored in acid-washed polycarbonate jar. The collected samples were immediately frozen with dry ice and transferred to laboratory for analysis

Sediment core samples were taken with SCUBA diving using an acryl barrel (length 50 cm, internal diameter 12 cm). The tubes were manually sunk into the sediment to obtain 20-40 cm long cores depending on the site. The core was sectioned in 2 cm interval with stainless plates. Only the central part was sampled to avoid possible contamination from the corer. Collected samples were frozen and later freeze-dried. Depth of sediment core was counted from the surface.

Analytical Procedure

The analytical procedure used on the sediment sample is a modification of the method suggested by Stallard *et al.* (1989). Air-dried sediments were ground and weighed to about 5 g in 50 mL polypropylene centrifuge tubes. Tripentyltin chloride was added to samples as a surrogate recovery standard. The samples were digested with 10 ml of 6 N HCl and subsequently extracted with 20 ml methylene chloride by shaking for 3 h. After 10 min centrifugation (4000 rpm), 2 ml of organic extracts were transferred to 15 ml glass test tubes and concentrated to about 25 ml under a gentle stream of nitrogen. Then the samples were resuspended in 2 ml *n*-hexane and derivatized with 250 μl of 2 M hexylmagnesium bromide for 20 min. The remaining Grignard Reagent was neutralized with 4 ml of 0.4 N sulfuric acid. The organic phase was recovered by centrifugation and cleaned up on 2 g of activated florisil. During the clean-up, the organotin compounds were eluted with *n*-hexane. The cleaned extracts were concentrated again and spiked with tetrabutyltin as an internal standard, and then analyzed by gas chromatograph (Hewlett Packard 5890 Series II) equipped with a capillary column (SPB-1, 30 m x 0.25 mm i.d. x 0.25 μm film thickness) and a flame photometric detector. A filter with a range from 625 to 2000 nm (Dietrich Optical) was mounted on the flame photometric detector. Under splitless injection mode, 2 μl of sample were injected. The gas chromatograph operating condition and quality assurance and quality control of the procedure were reported elsewhere (Shim *et al.*, 1999). Concentration of organotin compounds is expressed as ng/g of Sn on a dry weight basis to allow direct comparisons of the organotin compounds.

RESULTS

Occurrence of butyl- and phenyltins in surface sediment

Butyltin compounds were detected from all sites surveyed. TBT, dibutyltin (DBT), and monobutyltin (MBT) concentrations ranged 26 - 13300, <1 – 5090 and <2 – 1390 ng/g, respectively. The highest TBT, DBT and MBT concentrations were found in front of repairing shipyard in Ulsan Bay (St. 5 in Fig. 3), at which total butyltin concentration (sum of TBT, DBT and MBT concentrations) reached up to 19780 ng/g. The concentration of TBT accounted for the largest portion (69%) of total butyltin composition, and it was followed with DBT (20%) and MBT (11%).

Phenyltin compounds were detected at the only 11 out of 15 sites. TPT, diphenyltin (DPT) and monophenyltin (MPT) ranged <5 – 308, <4 – 103 and <3 – 339 ng/g, respectively. Mean total butylltin concentration (4313±6347 ng/g) was 33 times higher than that of total phenyltin (98±191 ng/g). Mean percent composition of each phenyltins was 33% for TPT, 15% for DPT and 50% for MPT.

Horizontal distribution of butyl- and phenyltins in surface sediment

Horizontal distribution of BTs in Ulsan Bay was quite different from the other harbors surveyed in this study, because exceptionally elevated TBT, DBT, and MBT concentration was found at St. 5 in front of the largest repairing shipyard in Korea (Fig. 3). Even though TBT concentrations at Sts. 1 through 6 exceeded 600 ng/g and began to decrease from St. 6 toward outer stations, positive

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TBT gradient shown from Sts. 1 through 5. Relatively high concentrations were found at St. 2 (938 ng/g) and St. 3 (1030 ng/g) compared to St. 1 (649 ng/g) and St. 4 (984 ng/g) at which harbors are located, respectively. Mean TBT percent composition in Ulsan Bay was 67%. Phenyltin compounds were detected from 8 out of 10 stations in Ulsan Bay. All the highest TPT, DPT and MPT concentration were detected at St. 5 same as BTs (Fig. 4). Horizontal distribution of TPT was similar to TBT in Ulsan Bay. TPT concentration showed negative gradients from St. 5 to St. 1 as well as from St. 5 to outer stations. Although three PTs were detected at Sts. 4, 5, and 6, the only high MPT (213 ng/g) concentration was found at St. 1.

Inside of breakwater in Okpo Bay, 11700 and 9190 ng/g of TBT were detected at Sts. 1 and 3, respectively, close to dry-docks of the shipyard (Fig. 5). These TBT concentrations were the second and the third highest among the 15 stations in this study. All of those exceptionally high TBT concentrations were found near shipyard. St. 4 also had 4300 ng/g of high TBT concentrations, whereas 1210 ng/g was found at St. 1. DBT and MBT concentrations were also relatively high at Sts. 1, 3 and 4. High mean TBT percent composition (74%) at five stations indicated that TBT compound has been freshly input in this area. Phenyltin compounds were also detected from Sts. 1, 3 and 4 (Fig. 6). TPT concentrations were 40 ng/g at Sts. 1 and 3, respectively. Distribution of total concentrations of PTs at the three stations showed similar trend to that of BTs.

Vertical distribution of butyl- and phenyltins in sediment core

TBT concentration of the core from St. 5 (UL) in Ulsan Bay exceeded 5000 ng/g at all depth (Fig. 7a). Exceptionally elevated TBT concentration (46100 ng/g) was found at the surface of UL and thereafter the concentration decreased markedly with depth.

A core was sampled in front of a shipyard in Okpo Bay (OP). Elevated TBT concentration of about 9000 ng/g was detected near surface and it was steeply decreased to a depth of 38-40 cm (Fig. 7b). Three butyltin concentrations were in order of TBT > DBT > MBT. Percent TBT composition was higher than 60% from the surface to a depth of 20-22 cm.

While TBT concentration in 2 cores showed decreasing profiles from surface to a certain depth, the decreasing trend in TPT was seen in a core from Okpo Bay (Fig 8b). The TPT profile of UL was quite different from that of TBT (Fig. 8a). A subsurface maximum was found at a depth of 12-14 cm in UL. The only OP showed a near surface maxima of TPT concentration and then the concentration decreased with increasing core depth (Fig. 8b).

Half-life of tributyltin and triphenyltin in sediment

Half-life of TBT and TPT in sediment was estimated from profile of these compounds in undisturbed cores and sedimentation rate. Model assumptions were that the sediment and organotin fluxes were constant and that the only loss mechanism for organotin was via degradation *in situ*. Acknowledging that the greatest source of uncertainty is the sedimentation rate, this simple model can be utilized to calculate the degradation rate in 2 cores for TBT and a core for TPT.

Sedimentation rates were estimated based on ^{210}Pb activity profiles. Table 1 lists statistical information, together with the estimated degradation rates and half-lives. The half-lives for TBT in UL and OP were 9.9 and 2.6 years, respectively. The half-life of TPT in OP was 3.1 yr.

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RESULTS AND DISCUSSION

Shipyards are thought to be primary sources of TBT and TPT in the coastal environment of Korea as in other coastal areas (*e.g.*, Tolosa *et al.*, 1992; Yonezawa *et al.*, 1993). Overall TBT concentrations in sediments are comparable to those in Porutuguese coastal environments (1–520 ng Sn/g) (Cortez *et al.*, 1993). Page *et al.* (1996) reported the similar range of TBT concentration (24–2760 ng TBT/g) in sediments from South Portland, Maine, U.S.A. TBT concentrations ranged from <1.5 to 1300 ng Sn/g except a ship repair area (3300±390 ng Sn/g) of Puget Sound (Krone *et al.*, 1989). Tolosa *et al.* (1992) also reported maximum TBT concentration near dry-dock harbor up to 9260 ng/g and at the other sites, the concentrations ranged up to 2420 ng/g in western Mediterranean coast. In this study, exceptionally higher TBT concentrations were found at the sites near shipyard. These results support that dry-docking activity is one of major sources of TBT compound.

When the number or tonnage of ships arrived each harbor was compared, the contribution of shipyard on TBT contamination was much higher. Ships arrived in Okpo Bay was 3,059,647 in tonnage and 951 in number in 1997 (MOMAF, 1997). However, TBT in sediment from Okpo Bay was 4 times higher than that of Pusan Harbor (MOMAF, 1998) in which 205,216,729 tons of and 33,557 of ships were arrived in the same period. Both the bay and harbor were almost blocked with breakwaters. These results support the significant input of TBT from shipyard during new application or removal of antifouling paints on or from ships.

Despite the well-known toxicity and the significantly long half-life of TPT in the marine environment (Fent, 1996), as well as the existence of analytical procedures for its determination in aquatic matrices, its occurrence in marine sediment has been reported by only Tolosa *et al.* (1992) and Gomez-Ariza *et al.* (1998). Phenyltins

were not detected in seawater and TPT was detected up to 11 ng/g from the Huelva coast, Spain (Gomez-Ariza *et al.*, 1998). Although Tolosa *et al.* (1992) also reported low TPT concentrations compared to that of TBT in western Mediterranean coastal enclosures, TPT was detected up to more than 200 ng/L in seawater and 4000 ng/g in sediment at several sites near marina. In this study, TPT was detected up to 308 ng/g in surface sediment and up to 4390 ng/g in sediment core, which are comparable to those mentioned above. Significant correlation between TBT and TPT concentrations in surface sediments and sediment cores where TPT was detected indicates that antifouling paint contribute to source of TPT compound in the marine environment. However, horizontal and vertical distribution of TPT in sediment is not as clear as that of TBT. Therefore, further study is required to identify TPT sources other than antifouling paint and to evaluate factors affecting its distribution.

The risk to the environment from TBT and TPT use is a function of both the toxicity of the chemical and its persistence and behavior in the environment. When a chemical is subjected to rapid degradation, calculation of its risk to the environment is especially sensitive to factors other than toxicity. Previous work indicates that TBT is fairly rapidly degraded in marine waters. Half-life of TBT in seawater is from several days (Seligman *et al.*, 1988) to several months (Maguire and Tkacz, 1985). However, as TBT shows a tendency to accumulate in sediments, TBT degradation processes in sediments are more likely to control the overall persistence of TBT in the environment. It becomes increasingly apparent from various recent studies that the degradation of TBT in sediments is a very slow process (Maguire and Tkacz, 1985; Fent and Hunn, 1991) with half-lives in the range of years (de Mora *et al.*, 1989; Watanabe *et al.*, 1995). The half-lives of TBT (2.6 and 9.9 yr) and TPT (3.1 yr) estimated from sediment core profile in this study are more or less higher than those of estimated from

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laboratory experiment (0.3 – 2.2 yr) (Watanabe *et al.*, 1995) and from core profile (2.6 yr) (de Mora *et al.*, 1995). However, no data is available to compare degradation and half-life of TPT in sediment.

The microbial degradation of TBT and the biochemical pathways involved are poorly understood, and thus investigations into the degradation of TBT in sediment should be carried out in more detail, under both aerobic and anaerobic conditions. Preliminary data from laboratory experiment indicated that the degradation in anaerobic sediment layers was much slower than under aerobic conditions (Yonezawa *et al.*, 1994). Page *et al.* (1996) reported that elutriating study of sediment from shipyard resulted in elevated TBT concentrations in seawater over water quality standard (2 ng/L) (Waite *et al.,* 1991). Therefore, desorption of TBT from contaminated sediment (Watanabe *et al.*, 1995), enhanced TBT concentration in surface sediment and cores, and considerable persistency of TBT in anaerobic sediment could be a concern on efficiency of regulation on use of TBT based anti-fouling paint.

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Table 1. Statistical parameters, sedimentation rate, degradation rate and half-life of TBT and TPT in sediment.

Core	N	Sedimentation rate (cm/yr)	k (yr-1)	$T_{1/2}$ (yr)	r2
Tributyltin					
UL	9	0.58	- 0.060	9.9	0.90
OP	16	1.07	- 0.266	2.6	0.98
Triphenyltin					
OP	9	1.07	-0.221	3.1	0.74
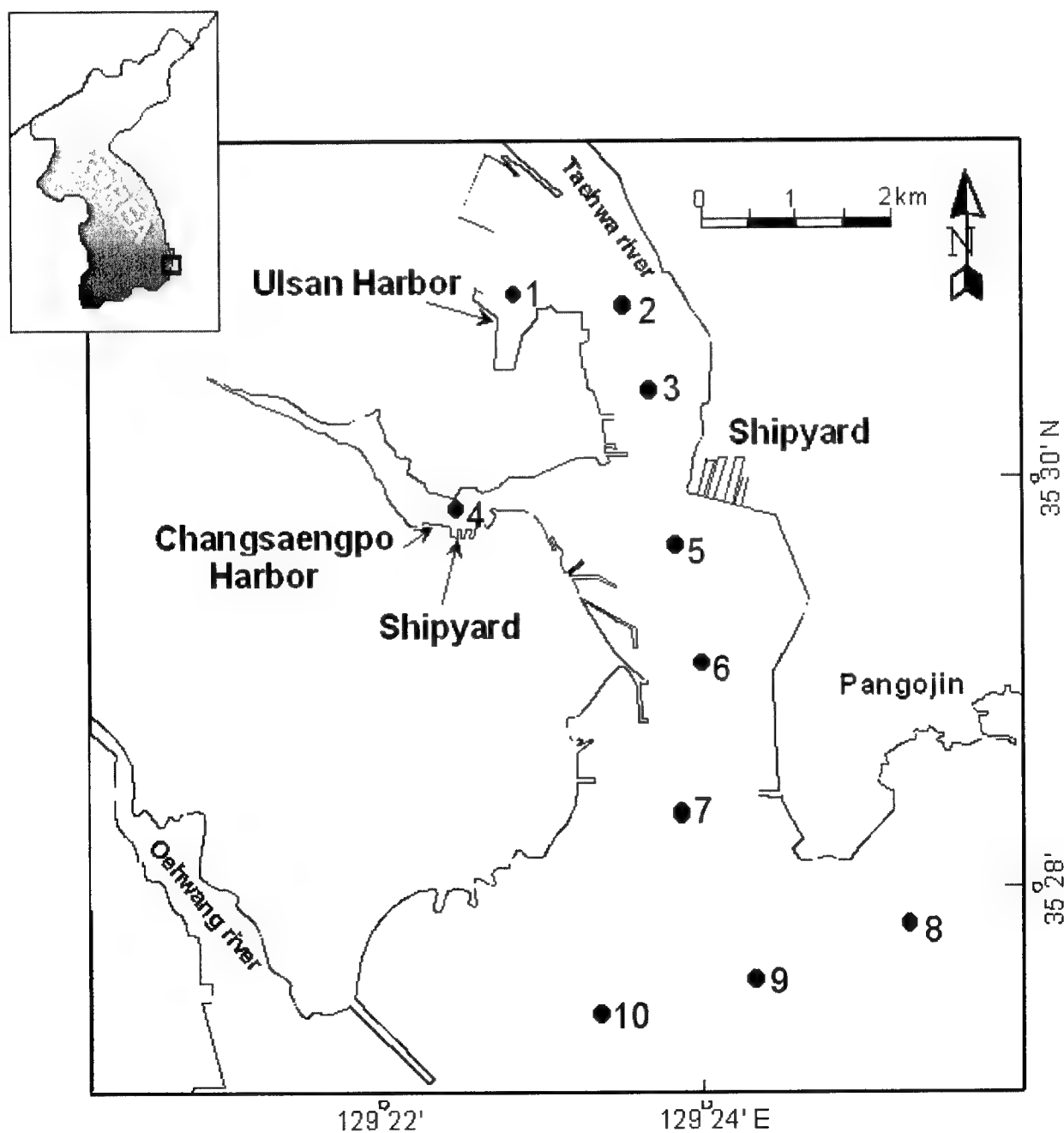
Fig. 1. Location of sediment sampling stations in Ulsan Bay
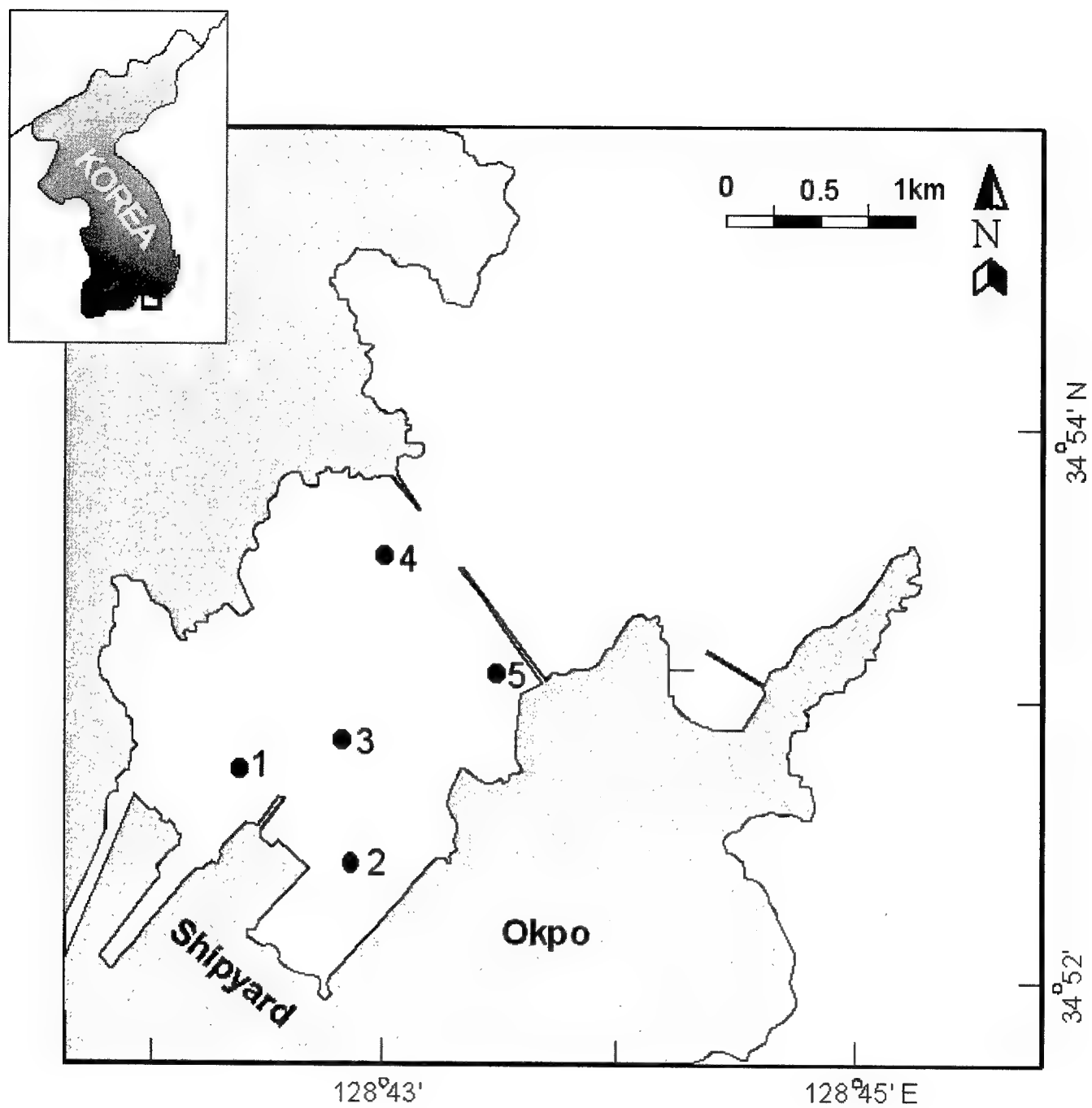
Fig. 2. Location of sediment sampling stations in Okpo Bay
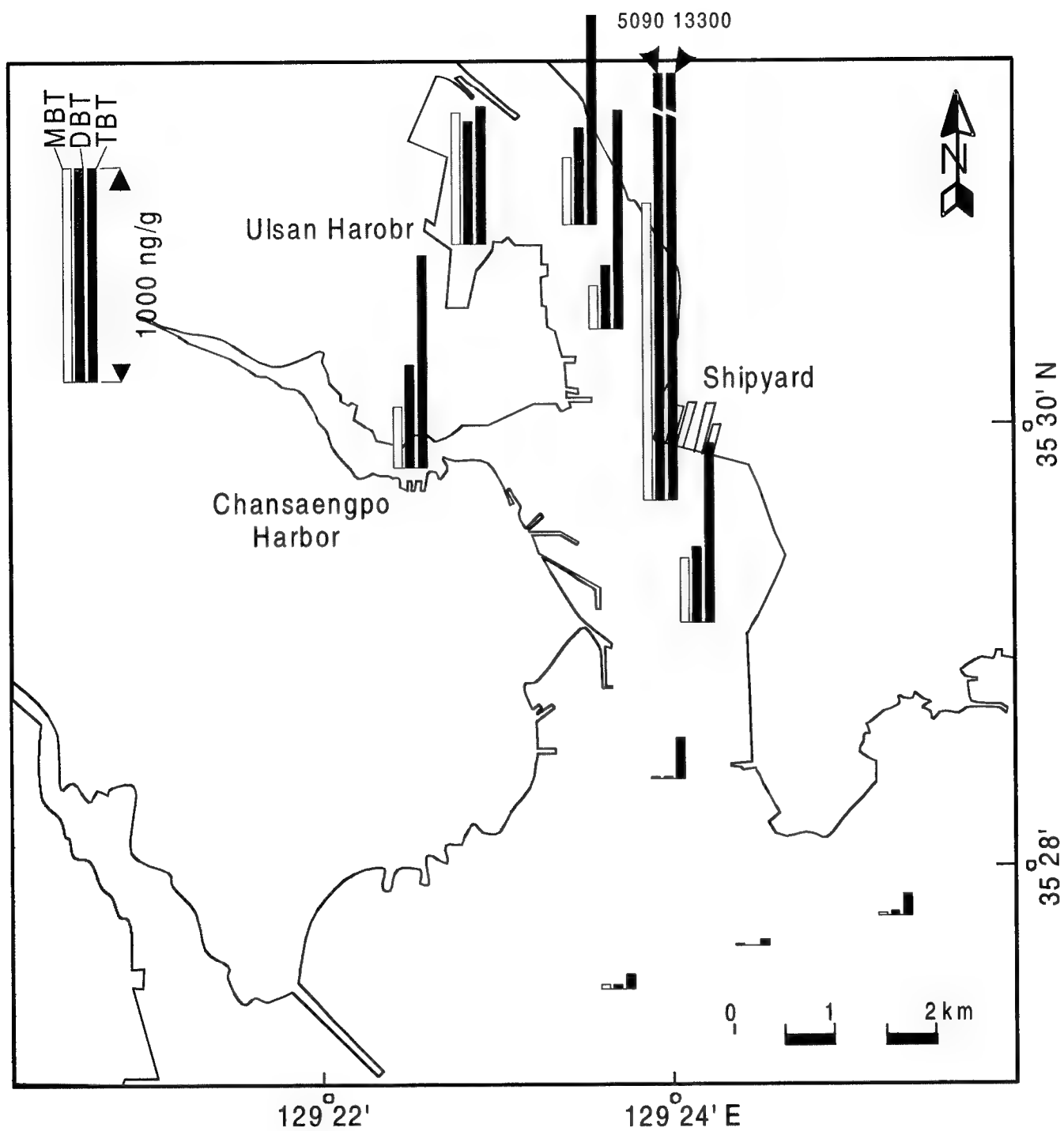
Fig. 3. Butyltin concentrations in surface sediment from Ulsan Bay
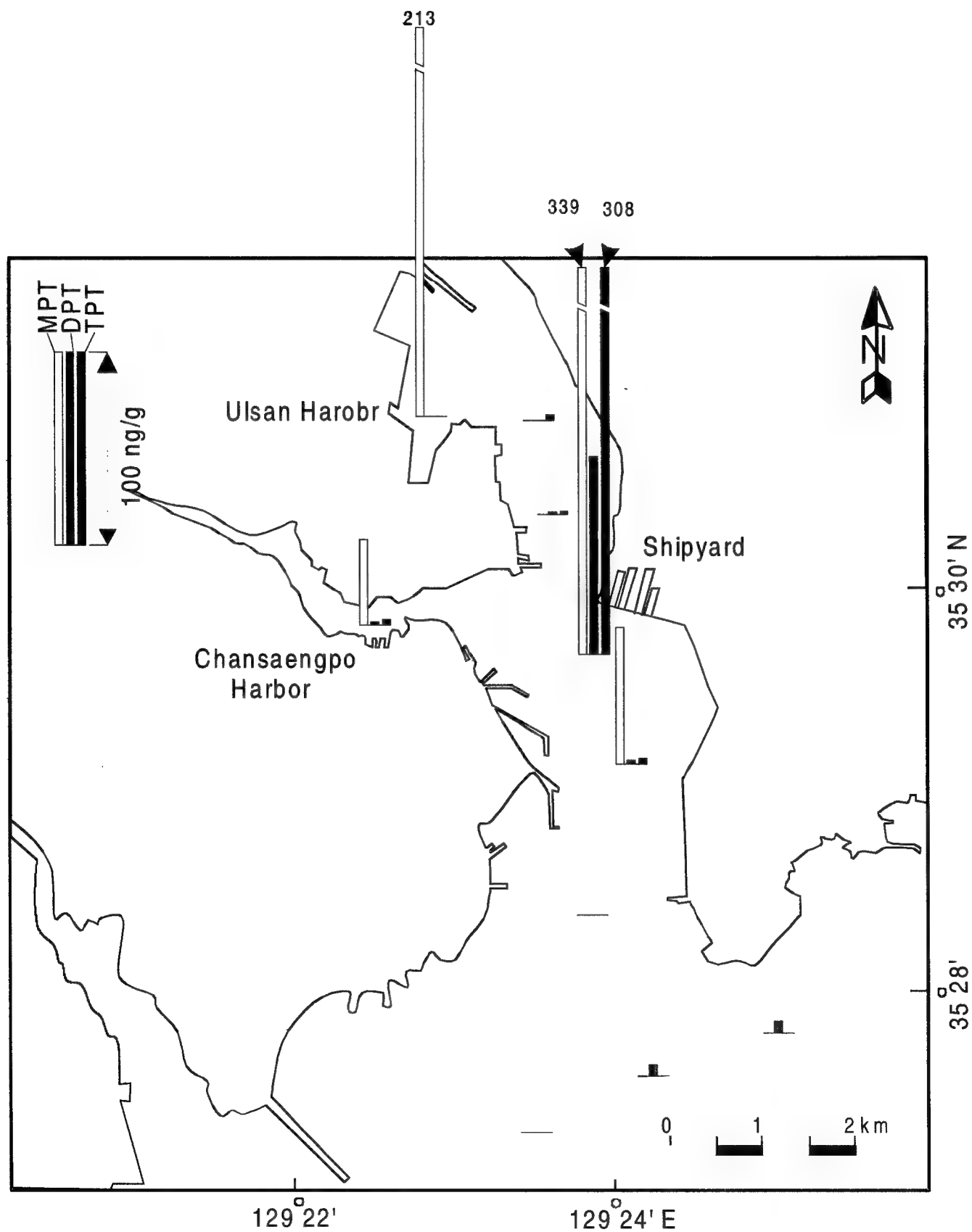
Fig. 4. Phenyltin concentrations in surface sediment from Ulsan Bay
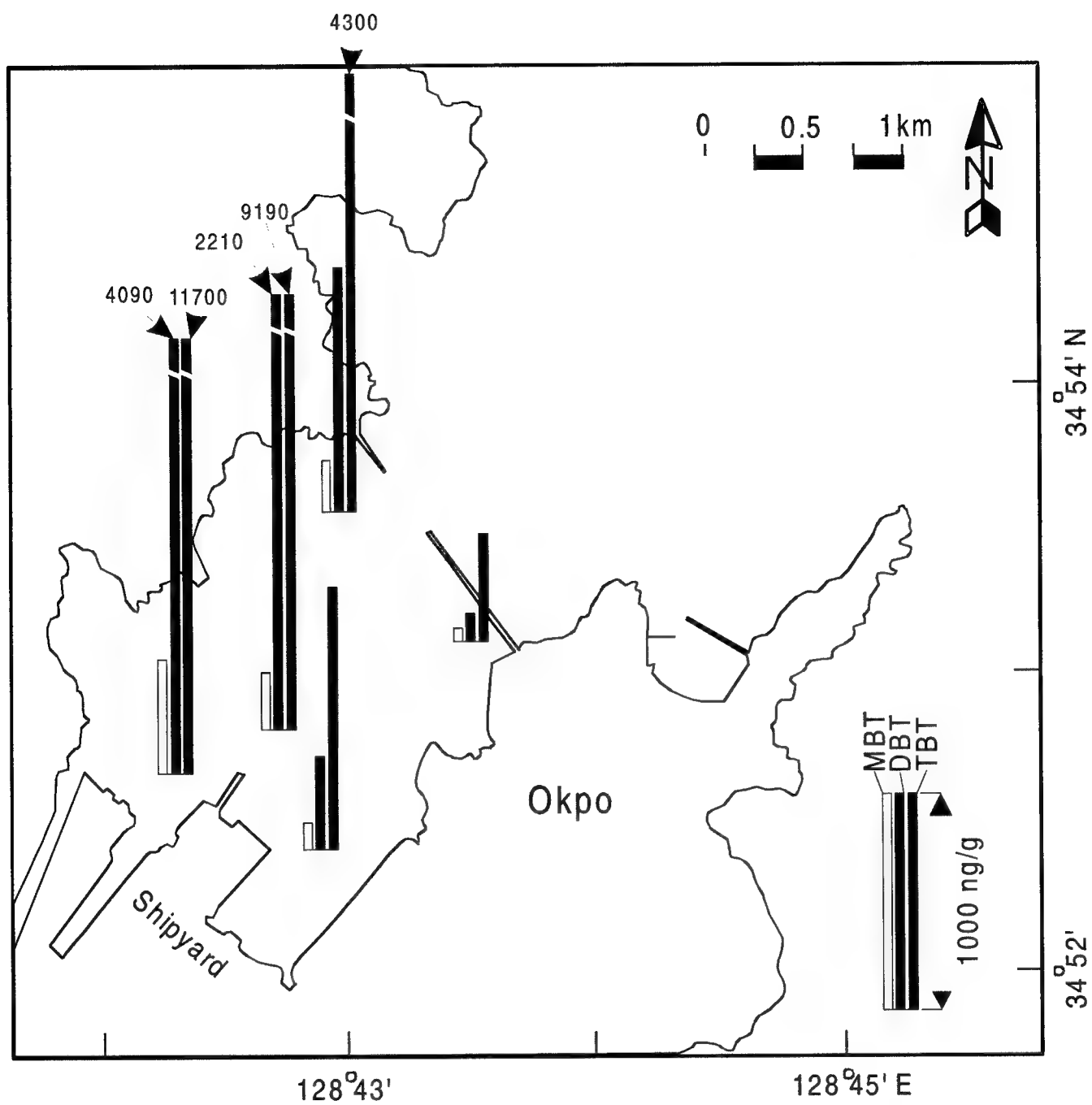
Fig. 5. Butyltin concentrations in surface sediment from Okpo Bay
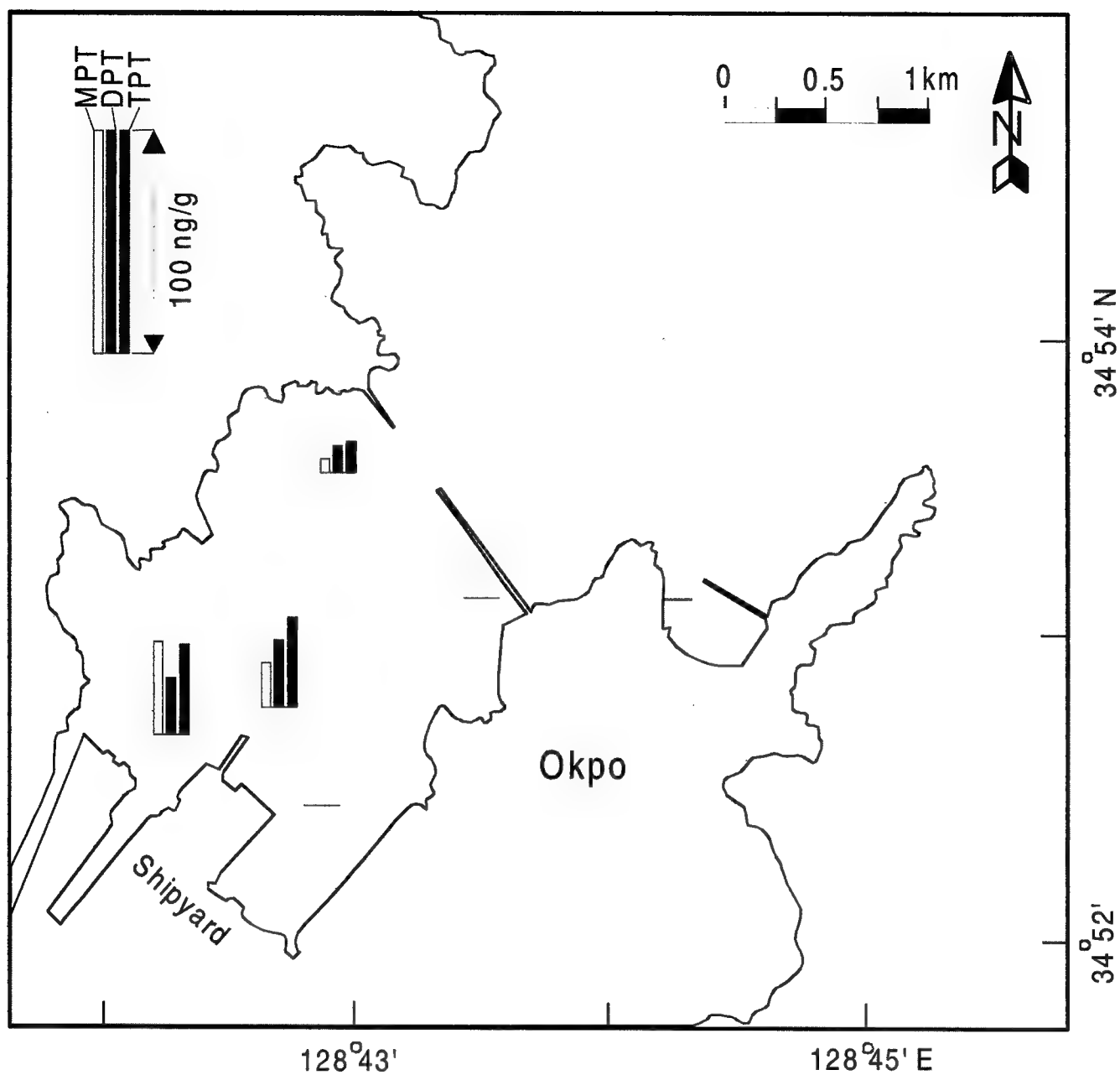
Fig. 6. Phenyltin concentrations in surface sediment from Okpo Bay
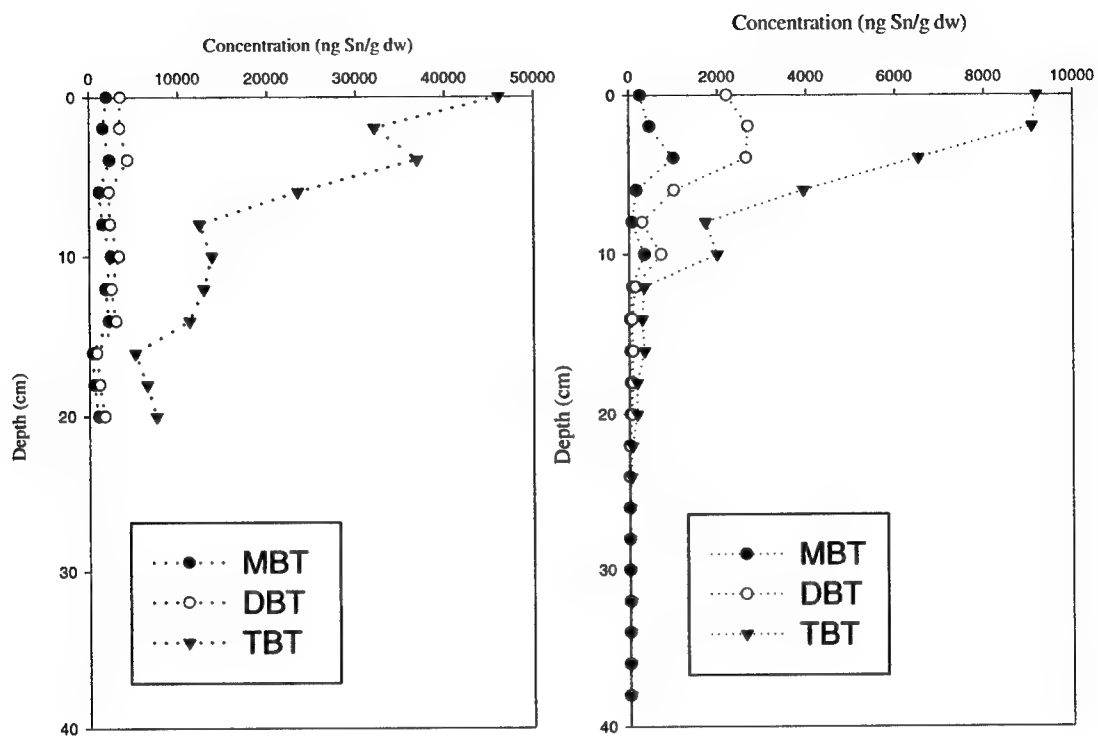
Fig. 7. Butyltin concentration profiles in cores from Ulsan Bay (a) and Okpo Bay (b)
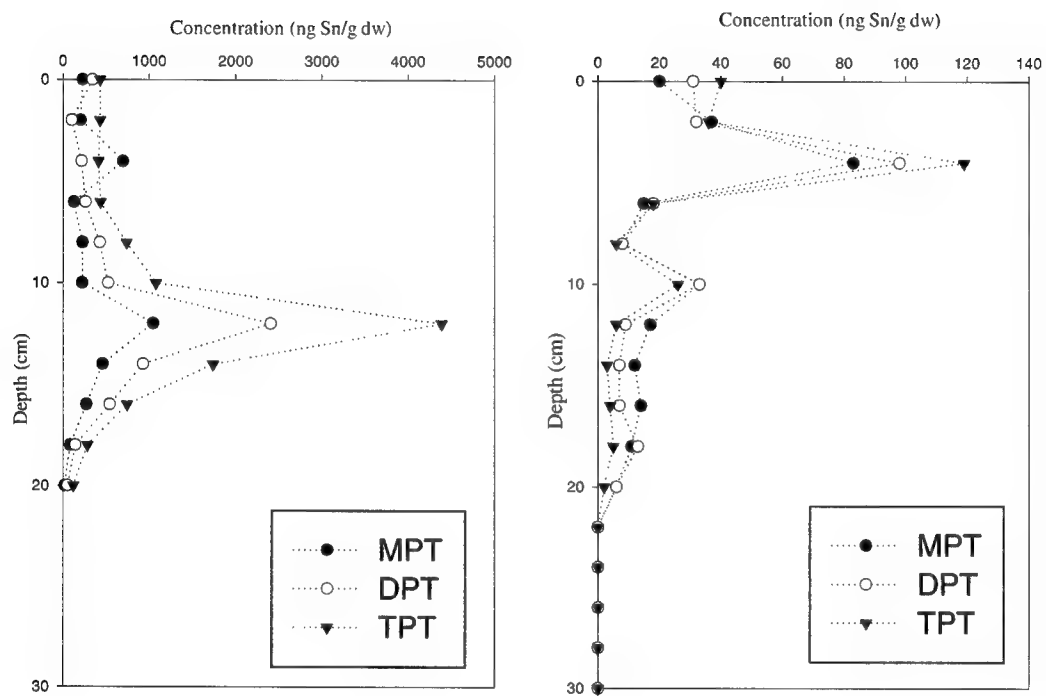
Fig. 8. Phenyltin concentration profiles in cores from Ulsan Bay (a) and Okpo Bay (b).

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Overview of Stormwater General Sector Permits for Shipyards: A Federal Perspective

Joel H. Salter Jr.[1]

ABSTRACT

An overview of the U.S. Environmental Protection Agency (US EPA) National Pollutant Discharge Elimination Program and NPDES Discharge Permits from a Federal perspective. For an extensive discussion or the EPSA NPDES Permit Program and NPDES Discharge Permits, see the EPA home page at http//www.epa.gov.owm. Here you will find general information and links to specific information. It is even possible to obtain copies of the storm water general sector permit for shipyards from the Federal Register online.

Keywords: Storm Water, Discharges, Shipyards, Drydocks, EPA, National Pollutant Discharge Elimination Program and NPDES Discharge Permits.

INTRODUCTION

Under the Clean Water Act Section 402 Congress has appointed to the Administrator of the EPA the authority to implement a permit program designed to reduce if not eliminate the discharge of harmful pollutants into waters of the US.

What is NPDES?

This program is the National Pollutant Discharge Elimination Program (NPDES). It requires that all point source dischargers apply for a permit to discharge.

- You are required to have a permit if you have a discharge of pollutant via a man made conveyance to a water of the US; and

- The discharger must obtain a permit from EPA or an approved State permit program. Currently 44 of the 50 states are authorized to administer their own "State" permit programs.

What is a Permit?

- It is a license;
- Issued by the government to persons conducting business in the U.S;
- Granting permission to do something which would be illegal in the absence of the permit;
- There is no right to a permit and it is revocable for cause (noncompliance); and
- Therefore an NPDES permit is a license to discharge and is renewed every five years.

The Scope of the NPDES Permit Program?

- There are Municipal permits and Non-municipal permits; and
- Shipyards are issued primarily Non-municipal discharge permits.

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Types of Discharge and Associated Regulations

Process Waste Water:
- 40 Code of Federal Regulations (CFR) 122
- 40 CFR 125
- 40 CFR 405-499

Non-Process Wastewater:
- 40 CFR 122
- 40 CFR 125

Storm Water -Storm Water Program:
- 40 CFR 122
- 40 CFR 125

There is also a General Storm water permit developed for Shipyards, published in the Federal Register (FR) Vol. 60. No. 186, Friday September 29, 1995, Notices Q and R.

Q) Storm Water Discharges Associated with industrial activity form water transportation facilities that have vehicle maintenance shops and/or equipment cleaning operations.

R) Storm Water Discharges Associated with industrial activity from ship and boat building or repair yards.

An Overview of the Science and Regulation of TBT and the Potential for Future Liability for Contaminated Harbor Sediments

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ABSTRACT

A draft Assembly Resolution prepared by the Marine Environmental Protection Committee (MEPC) of the International Maritime Organization (IMO) to propose a global ban on the use of organotins in antifouling paints was approved by the IMO Assembly at its 21st Regular Session (November 1999). In approving the Resolution, the Assembly agreed that a legally binding instrument (global convention – an international treaty) be developed by the Marine Environment Protection Committee that should ensure by January 1, 2003 a ban on the application of Tributyltin (TBT) based antifouling paints and January 1, 2008 as the last date for having TBT-based antifouling paint on a vessel. The Assembly also agreed that a Diplomatic Conference be held in 2001 to consider the adoption of the international legal instrument. Monitoring, policing, enforcement, fines and record keeping are yet to be defined. In addition, the MEPC has also proposed that IMO promote the use of environmentally safe anti-fouling technologies to replace TBT.

In the U.S., existing coastal zone, federal and state regulations have had a significant impact on reducing TBT levels, generally to well below the provisional water quality standard of 10 ng/L, and in bivalve tissues. Current environmental and marine and estuarine water concentrations are well below predicted acute TBT toxicity levels. Estimation of chronic toxicity effects using mean water TBT concentrations indicate that current levels would be protective of 95% of species. Analysis of allowable Daily Intake/Oral Reference Dose Values from market basket surveys and the NOAA National Status and Trends data suggest that there is no significant human health risk from consuming seafood contaminated with TBT. Most of the data that exceeded these values were from areas of high TBT input from ports, harbors and marinas (commercial shipping, shipyards and drydock facilities) and sites of previous contamination. In the U.S., at this time, TBT environmental data and lack of acceptable alternatives does **not** justify a global ban for TBT.

This papers presents a discussion of: (1) Global environmental TBT concentrations and exceptions, (2) Comments on the scientific basis for the regulation of TBT, (3) The TBT scientific controversy, (4) Antifouling biocides and invasive species, and (5) The potential liability to shipping industry, shipyards and paint manufactures from the global ban on TBT in antifouling paints.

Keywords: Tributyltin, TBT, biofouling, antifouling marine coating, regulation, policy, toxicity, invasive organisms, liability and contamination of dredged materials.

GLOBAL ENVIRONMENTAL CONCENTRATIONS A DECADE AFTER REGULATION

In the United States, since the passage of the Antifouling Paint Control Act of 1988, the environmental concentrations of organotin compounds have declined (Seligman et al., 1990; Wade et al., 1991; U.S. EPA, 1991; Valkirs et al., 1991 and Huggett et al., 1992). Three national and regional monitoring programs in the U.S. have sampled for TBT since the passage of OAPCA in 1988. These are the U.S. National Oceanic & Atmospheric Administration's (NOAA) National Status and Trends Monitoring

(NS&T) Program, which was created in 1984 (see O'Connor, 1998. Overviews are presented in the Proceedings of the Coastal Zone 93 and the special issue of MPB Vol. 37 No. 1 (O'Connor and Pearce, 1998) and the papers there in. A second TBT monitoring program was the U.S. Navy Long-term Monitoring Program associated with Navy home ports and harbors (See U.S. Navy, and EPA, 1997). The third monitoring program is the consortium of tributyltin manufactures (ORTEPA) Long-term Monitoring Program contracted to Parametrix Inc., with results published in Cardwell et al., (1997; 1999); ORTEPA (1997, 1998). The results of these three national monitoring programs have been compared by Russell et al. (1998) who found that all of these programs have found declining environmental concentrations of TBT over time since the enactment of OAPCA in 1988. Water concentrations have declined 56% - 71%, sediment 47% -55% decline, and bivalve tissues 40%-82% within a few years. Mean TBT concentrations in water are generally below the current U.S. EPA marine chronic water quality criterion of 10 ng/L (Russell et al., 1996).

Studies have found that mean TBT surface water concentrations have significantly decreased in San Diego Bay, following legislative restriction on the use of organotin antifouling paints in California. Regression analysis of the San Diego data suggests that surface water concentrations would decrease by 50% in 8 to 24 months. It was found that sediment TBT concentrations in San Diego Bay did not reflect recent decreases in water column values and were variable among stations over time, and that tissue concentrations in *Mytilus edulis* have generally declined in San Diego Bay since February 1988 (significantly since April and July 1990), Valkirs et al. (1991).

Similar findings have been reported for the Chesapeake Bay by Huggett et al. (1992) for the Hampton, Virginia area of the Bay. Surface water samples analyzed after the passage of the Organotin Antifouling Paint Control Act (OAPCA) of 1988 in marinas and yacht clubs indicated that TBT concentrations had significantly decreased when compared to results of earlier studies by Huggett (1986, 1987) and Huggett et al., (1986), U.S. EPA Chesapeake Bay Program, (1987), and Hall (1986; 1988); Hall et al. (1986; 1987).

The EPA Report to Congress (U.S. EPA, 1996) is a summary of the status of development of alternatives to TBT. The driving force is to develop an alternative to TBT, which could compete in the $ 500 million per year total antifoulant paint market (C&E News, Oct 14, 1996). The TBT copolymer used in deep-ocean going vessels represents between 65-70 percent of this market. The goal is to develop a non-toxic (no effect on non-target organisms) antifoulant, which effectively inhibits the formation of biofilms and prevents biofouling. The major finding of the EPA 1996 Report (which has not been updated) was that "an alternative antifoulant as effective as TBT self polishing copolymer paints has not been found." They also reported that the principal alternatives today to TBT antifouling paints are copper-based. However, hulls treated with copper-based paints were reported to foul within 15 to 18 months due to formation of a "green layer" on the surface of the hull. The green layer is the reaction of copper to seawater, which results in the formation of a coating of insoluble cupric salts, preventing the release of copper from the paint underneath. Once the green layer is present, the antifoulant protection is no longer effective. Underwater hull scrubbing is required to remove the green layer and attached fouling organisms and with frequent scrubbings, the period of protection can be extended for up to 30-36 months depending on water temperatures. Revised estimates on fuel savings from the use of TBT by the Navy ranged from 18 to 22 percent of the total fuel consumption (U.S. EPA, 1996).

EPA has recently noted that noted that the use of copper is coming under increasing regulatory pressure with some coastal states restricting the amount of copper that may be discharged into local harbors during hull cleaning and washing. These regulations may impact the U.S. Navy's use of copper in antifoulant paints and leave the Navy without alternatives that meet their requirements. The Navy has held a workshop on the chemistry, toxicity and bioavailability of copper and its relationship to regulation in the marine environment to improve the scientific understanding of copper in the marine environment and attempt to develop a solid scientific basis for future approaches to copper regulation (Seligman and Zirino, 1998). In addition, the Navy has funded the development of in the water cleaning systems for copper that also collect all waste and wastewater for treatment (Bohlander &

Montemarano, 1997). It also should be noted that both Holland and Sweden have recently introduced regulations on antifouling paints for pleasure vessels containing copper as effective September 1, 1999. Canada has set the release rates of copper in antifouling paints at 40 mg/cm^2/day. Copper is a potential toxin to marine organisms (Lewis and Cave, 1982; and Goldberg, 1992). It should also be noted that the U.S. Department of Defense and the U.S. Environmental Protection Agency have been working on the Uniform National Discharge Standards (UNDS) which will regulate the amount of biocidal discharges from antifouling coatings into the sea by December 2000, with the current release rates under consideration for copper less than the 40 mg/cm^2/day. (see UNDS Website: http://206.5.146.100/n45/doc/unds/SITEMAP/ITEMAP.HTML).

TBT concentrations in water, sediment, and biota have generally declined. Evans (1999b) has an excellent summary paper on the concentrations and environmental effects as a measure of the effectiveness of national regulations. TBT concentrations in surface marine waters have declined in Arcachon Bay, France (Alzieu et al., 1986, 1989) and in the UK (Cleary, 1991; Waite et al., 1991, 1996; Dowson et al., 1992, 1993a, 1993b and 1994) the USA (Valkirs et al., 1991; Huggett et al., 1992, 1996; and Uhler et al., 1993) and in the Gulf of Mexico from Wade et al., 1991; and Champ and Wade, 1996; Garcia-Romera et al., 1993) and Australia (Batley et al., 1992). Tissue concentrations in molluscs have declined (Valkirs et al, 1991; Wade et al., 1991; Champ and Wade, 1996; Waite et al., 1991, 1996; and CEFIC, 1994).

Exceptions to this general decline of TBT in bottom sediments have been reported as hot spots associated with ship channels, ports, harbors, and marinas in Galveston Bay (Wade et al., 1991), Hong Kong (Ko et al., 1995), the Netherlands (Ritsema et al., 1998), Iceland (Svavarsson and Skarphédinsdóttir, 1995) and in Israel (Rilov et al., 1999).

Oyster culture has recovered in France (Alzieu et al., 1986, 1989 and Alzieu, 1991 and 1996). In southern England, Waite et al. (1991; 1996; and Dyrynda, 1992) reported improved oyster culture. For Australia, Batley et al. (1992) have reported improvements in oysters. Minchin et al. (1987) have reported improvements for

scallops and Minchin, (1995) and for flame shells in Ireland.

The literature has also reported wide spread decline in Imposex and population recovery for dogwhelks (*Nucella* spp.): England (Evans et al., 1991; Douglas et al., 1993; Gibbs and Bryan, 1996a 1996b); Scotland (Evans et al., 1994 and 1996; and Nicholson et al., 1998); Ireland (Minchin et al., 1995); Norway (Evans et al., 1996); and Canada (Tester and Ellis, 1995; Tester et al., 1996).

COMMENTS ON THE SCIENTIFIC BASIS FOR THE REGULATION OF TBT

It is interesting to note, that the "movement" to regulate TBT based antifouling paints during the 1980's was initially based on "correlation" and "generality" type science (see Salazar and Champ, 1988). Peruse the bioassay discussions in White and Champ (1984), and see Evans et al. (1996) and Evans (1997 and 1999a; 1999b) for a discussion on Imposex. The Salazar and Champ (1988) paper was a preliminary review of the science that was prepared for an Oceans '88 conference proceedings to stimulate discussions. However, it was published about the same time that OAPCA was passed in the U.S. and interest in TBT and support for further research declined (Champ and Seligman 1996a). Fortunately this was not true on a global basis. Some of these concerns have been revisited and are discussed in a collection of papers reprinted and submitted by the paint industry to the MEPC by the Organotin Environmental Program Association (ORTEP, 1996, 1997 and 1998). Many of these points were discussed at the 1998 Annual Meeting of the American Chemical Society in Dallas (Rouhi, 1998) and in Champ (1998). In addition, papers were presented at the Oceans '99 Conference in Seattle (September, 1999) that discussed the science being used in the regulatory process (see Brancato and MacLellan, 1999; Cardwell et al., 1999; Damodaran et al., 1999; Evans, 1999c; Evans and Nicholson, 1999; Evans and Smith, 1999; MacLellan et al., 1999; and Toll et al., 1999). Several of these papers delineate problems with data quality and quantity, protocols and question the emphasis of the data and the information that is being utilized as a basis for proposed additional regulation. *However, these*

points are moot if comparable and environmentally friendly alternatives to TBT are available and acceptable (Champ, 1998, 2000).

The Scientific Controversy

Early concern was expressed that most of the evidence the regulatory process considered to be significant came from bivalve mollusks: (1) it was believed that mollusks were more sensitive than other animal groups to TBT, (2) Many bivalves have a cosmopolitan distribution and are commonly maintained in the laboratory, (3) filter-feeding bivalves may be more susceptible to TBT due to their feeding strategy, and (4) many bivalves have an economic importance in the commercial shellfish industry (Champ and Seligman, 1999b; 1999c). A significant and subtle distinction that needs to be kept in mind is the difference between the environmental impact of TBT on the shellfish industry and the environmental impact of TBT on natural shellfish populations. The point is that the effects on cultured shellfish do not necessarily demonstrate similar ecological effects in a typical natural situation. A second point is related to public definition of "acceptable" land use. It is difficult to appreciate being interested in culturing shellfish in areas adjacent to marinas and shipyards given their history of being defined as "polluted" due to acute and chronic contamination problems (Champ, 1983). Ports, harbors, and marinas are publicly approved marine land uses. These facilities are usually located in highly protected areas with low flushing rates, long water mass retention times, oil spills, high levels of contaminants, and high silt loads which are not optimum conditions for culturing filter-feeding bivalves.

In Europe, the critical evidence for the initial regulations in the mid 80's, was associated with shell thickening in oysters (*Crassostrea gigas*) and imposex in dog-whelks (*Nucella lapillus*). In the U.S., the early critical evidence was associated with laboratory studies that reportedly demonstrated unacceptable effects on growth and development in oysters (*C. gigas, Ostrea edulis*) and clams (*Mercenaria*) (Champ, 1986). All of this evidence was based on only four species, a similar number of laboratory tests and field observations, generally unsupported by chemical measurements and not published in peer reviewed

journals. In general, the laboratory studies utilized questionable methodology and field studies lacked the necessary scientific rigor.

Bioaccumulation of TBT from Sediments

In what may become a classic regulatory textbook debate and case study, are the results of a 5-year study of TBT-contaminated sediments associated with an U.S. EPA Superfund site in Washington State. The issues unresolved are summarized in a U.S. EPA Region 10 Technical Memorandum (for addressing unanswered questions) that is entitled: "Topics Related to the Tributyltin Study at the Harbor Island Superfund Site, Seattle, Washington" (Keeley, 1999, Personal Communication). During EPA Superfund remedial investigations at the Harbor Island Site (Weston, 1994), TBT had been previously identified as a contaminant of potential concern due to elevated concentrations in the marine sediment (higher concentrations ranged from 10 to 50 ppm dw TBT).

Because there are no established Federal or State sediment quality guidelines or standards for evaluating TBT concentrations in sediment, the U.S. EPA formed an interagency working group to identify and evaluate approaches to deriving an effects-based sediment cleanup concentration for use at Superfund sites in Puget Sound, Washington. Most of the available literature presented toxicity of TBT for water, and only two studies (covering four species) evaluated toxicity associated with sediment concentrations of TBT (U.S. EPA, 1996a). The working group also proposed the calculation of an Apparent Effects Threshold (AET) value, which could be used as a sediment criteria for TBT, using available chemical (bulk sediment) and biological (sediment toxicity, benthic infauna) data from Puget Sound. The working group found that: (1) Existing Puget Sound data did not support a clear identification of an AET value for TBT; (2) A maximum no-effect concentration could often not be established because, in several cases, the highest sediment TBT concentration was associated with no biological effects and was also the highest concentration measured among all the stations sampled; (3) Good correlations were <u>not</u> found between bulk TBT sediment concentrations and laboratory toxicity and *in situ* benthic community responses; and (4) Based on an evaluation of available information, "bulk sediment concentrations of TBT were a poor

predictor of bioavailable TBT" (U.S. EPA 1996a). Further, the working group recommended, based on a general understanding of chemical partitioning and the lack of observed relationships between bulk sediment TBT and adverse ecological effects, that when TBT is a contaminant of concern in sediment, pore water concentrations of TBT should be measured, and toxicity testing or bioaccumulation testing (*in situ* or laboratory) be conducted to confirm the ecological significance of concentrations measured in pore water. The working group did not provide recommendations for specific bioaccumulation test species, because it was believed that additional work needed to identify the most appropriate species (ESI, 1999a).

In a series of subsequent TBT related studies, a consortium of Harbor Island waterfront property owners (the Port of Seattle, Lockheed Martin Corporation and Todd Shipyards Corporation) funded a study to evaluate the bioavailability of and the potential effects associated with TBT in sediments at the Superfund site. The overall purpose of this study was to develop a site-specific, effects-based TBT tissue trigger concentration that could be used to determine the need for remediation of TBT-contaminated sediments. In this study, effects considered relevant for the development of a site-specific tissue trigger value were mortality; reduced growth; and reproductive impairment. The normal TBT effects cited in the literature, such as bivalve shell thickening or induction of (early stage) imposex or intersex in meso- and neogastropods, were not appropriate in this evaluation, because (1) these biological responses do not have established connection to population-level effects, and (2) there is a lack of suitable habitat at the site for the species (oysters, mesogastropods, and neogastropods) typically affected by shell thickening, imposex and intersex. The study site is a deep (-30 to -60 ft mean lower low water), industrialized channel of subtidal sediments within the Duwamish River Estuary. Very little intertidal habitat is available, due to extensive channelization and dredging of the waterway, and no commercial or recreational shellfish beds occur. In addition, gastropods typically are not a large component of the benthic community at the site, and mesogastropods and neogastropods are very limited in abundance (ESI 1999a). The study was performed in accordance with a Sampling and Analysis Plan

(SAP), prepared by ESI (1998) that was reviewed and commented on by all reviewers prior to its approval by U.S. EPA, and resultant data from the TBT study were determined to be of high quality by EPA (ESI, 1999b).

The evaluation of TBT sediments from the Harbor Island sediments was conducted in two studies. First, a TBT literature review was conducted to identify global paired tissue residue and effects data for marine invertebrates and fish (ESI 1999a). The tissue residue data were used to estimate a site-specific, effects-based tissue trigger concentration for TBT (ESI 1999a). Second, sediment samples were collected throughout the study site for chemical and biological testing (ESI 1999b). TBT concentrations were measured in bulk sediments and pore water samples; a subset of sediment samples collected was used for bioaccumulation testing. With approval from all involved agencies and consistent with national guidance, bioaccumulation testing was conducted to determine site-specific exposures to two marine invertebrate species: (1) a bivalve (*Macoma nasuta*) and (2) a polychaete (*Nephtys caecoides*). No approved marine sediment toxicity bioassay protocols for test species that have demonstrated sensitivity to TBT were available (U.S. EPA, 1996a), so no toxicity testing was conducted. The resulting tissue TBT concentrations were then compared to the effects-based trigger concentration derived from the literature (ESI 1999b; Keeley, Personal Communication).

Results of this study were that the survival of the laboratory test organisms was high, and the lipid content of the organisms exposed to test sediments was similar to controls, which suggest to many of the projects reviewers that the organisms were in good physiological health during the exposure period. A site-specific tissue trigger (3 mg/kg DW TBT) was estimated (Meador, 2000) for the study site for evaluating bioaccumulation data from the study area, and for the 20 stations sampled and tested at the site, none of the tissue samples from the bioaccumulation tests exceeded the tissue trigger value of 3 mg/kg DW TBT. Thus, no cleanup of TBT sediments was recommended. The value of 3 mg/kg DW TBT, which was derived from paired tissue residue effects data in the literature, is estimated to be the tissue residue

associated with reduced growth in a number of invertebrate species. The level is however, very similar to the overall geometric mean of paired effect/no-effect data and the estimate of a sublethal effects level based on a multi-species acute-to-chronic effects ratio for the study area.

The development of tissue residue effects thresholds is part of EPA's overall strategy for management of specific contaminants in sediments in the US rivers and estuaries. The lack of TBT bioaccumulation from sediments in these studies is not understood, creating more unanswered questions and confusion in the data and suggests that further studies are needed prior to the development of a protocol for estimating TBT tissue level triggers for regulatory use. Results from the study also found that TBT tissue concentrations were most strongly correlated with dw-sediment and carbon-normalized sediment TBT concentrations, and there were weak correlations with filtered and unfiltered pore water TBT concentrations. If there is no relationship between levels in sediments and bioaccumulation levels in tissues, then the TBT in the sediments has been shown to not be bioavailable. For the determination of ocean dumping for dredged materials, the decision has to do with whether a species has accumulated more than 3 mg/kg DW TBT.

After completing the Harbor Island TBT bioaccumulation studies, the U.S. EPA (1999) prepared a Technical Memorandum to address topics of interest identified by EPA and other agency reviewers on issues related to the findings presented in the above study (ESI, 1999c). Several scientists reviewing the results of the Harbor Island studies had a difference of opinion in the interpretation of the results. Some reviewers of ESI (1999b) indicated that the measured TBT bioaccumulation in test organisms for this project was less than they would have expected from the measured sediment and pore water TBT concentrations in site samples. This concern was based in part on a comparison of the bioaccumulation test results with studies reported in the literature and with other similar studies performed in the general Harbor Island area. Some reviewers suggested that several test parameters (e.g., species selection, exposure regime of tests, organism health) might have influenced the results.

Salazar and Salazar (1999a, b, in preparation) in reviewing the Harbor Island bioaccumulation studies believe that the major lesson learned from this study and their separately conducted caged bivalve bioaccumulation studies are that lab tests don't predict nature very well, or adequately consider equilibrium and energetics. They have listed the following specific lessons learned from their research on TBT uptake by mussels that: (1) Lab tests generally over-estimate toxicity; (2) Lab tests generally under-estimate bioaccumulation; (3) Bivalves are sensitive test species; (4) Exposure period should be determined by equilibrium; (5) Growth rate affects bioaccumulation potential; (6) Quantifying health is important in data interpretation; and (7) Tissue chemistry can be used to predict effects. Salazar and Salazar (1987; 1989; 1996) and Salazar et al. (1987) have found that survival and growth effects of TBT were over-estimated based on laboratory tests and mesocosm studies. They placed caged mussels at the seawater intake to test tanks and found that growth rates were about 4 times faster outside the test tanks compared to growth in the control tanks.

In the Harbor Island studies, the issue is the interpretation of the tissue chemistry data and Salazar and Salazar (1996a b, in preparation) believe that, even though the U.S. EPA followed all state and national guidance and accepted state-of-the-art testing protocols, they believe that laboratory exposures have under-estimated bioaccumulation levels due to animal health from test conditions. Meador (Personal Communication) suggests that *Macoma* in these tests were more than likely ventilating clean overlying water, reducing its exposure to TBT. Generally speaking, bivalves are extremely sensitive to food and flow rate and growth rates seldom if ever achieve the growth rates of animals in nature. Laughlin (1996) reported that BCF is related to growth rate and that the highest growth rates were associated with the highest BCFs. Laughlin referred to this as the concentration dependence of TBT accumulation. Widdows et al, (1990) found that the operative mechanism is that growth rate is also related to filtration rate. Laughlin (1996) measured BCFs of only about 5,000 compared to an average of about 30,000 from Salazar (1989); and Salazar and Salazar (1996) transplanted mussels, suggesting that Laughlin's animals may have been under severe stress.

The 28 day exposure bioaccumulation tests in the Puget Sound Studies with the marine bivalve *Macoma nasuta* (which is a facultative feeder – both filter feeding and deposit feeder) did not reach steady state, when the test was extended to 45 days, and the results may have reflected test conditions in which *Macoma* may have been stressed. Originally, EPA proposed modifying the test procedure in accordance with Test Sediment Renewal (EPA Guidance Manual on Bedded Sediment Bioaccumulation Tests (EPA/600/R-93/183) which recommends complete sediment renewal for test longer than 28 days. Bruce Boese (EPA Newport Laboratory and an author of the manual) suggests that the primary reason for performing sediment renewal was to give the animals more "food". For the Harbor Island tests, it was decided to add 0.5 cm of sediment to the test chambers every 7 to 10 days for the entire test (overlaps weekends). Questioned in the study was also the use of lipid content at the beginning and end of the test was considered as an endpoint to evaluate potential stress on the test organisms. Boese (Personal Communication) felt that lipid content of Macoma does not give you any information about the health of Macoma, and that loss/gain of lipids is primarily related to reproduction.

Laboratory bioassays have become an environmental test industry and big business in making regulatory decisions. Their simplicity, cost and reproducibility are very attractive to regulatory policy and decision-makers. However, their scientific value or merit has been repetitively questioned. White and Champ (1983) addressed this issue of "The Great Bioassay Hoax" and Salazar (1986) asked similar questions regarding the application of traditional laboratory toxicity tests to assessments of TBT. Salazar and Salazar have raised these questions to a higher level of sophistication but the old problems still remain. Scientists in the bioassay testing business hesitate to challenge an accepted regulatory test, because of a lack of a replacement, and the process to get one accepted, but still need to strive to develop standardized tests that validate and represent what an organism actually experiences in the environment.

Salazar and Salazar (1999a, b, in preparation) also feel that the other interesting issue here is that they believe that the *Macoma* bioaccumulation test may be flawed for the following reasons: (1) since the ASTM

protocols do not require any effects measurements, one can never be sure of the health of the test organisms, (2) the largest and slowest-growing animals generally have the lowest tissue concentrations in transplant studies, and (3) people tend to forget that Macoma is a facultative deposit feeder, and can either filter- or deposit-feed. Recent summary papers have reported that many benthic invertebrates are quite plastic in their feeding mode and readily shift back and forth from filter- to deposit-feeding depending on local environmental conditions and available food and can select between clean and filtered seawater and highly contaminated sediment.

Langston and Burt (in preparation) found that concentrations in tissues of *Scrobicularia plana* (a deposit feeding clam) in the UK reached equilibrium in tissues after 40 days of exposure. They also reported that sediments are an important vector for TBT uptake in deposit-feeding clams. They also concluded that it is particulate rather than desorbed TBT, which is most significant. Laughlin (1996) reports that bioaccumulation factors appear to be high, but field studies, in particular, have not necessarily carefully characterized the route of uptake (water or food).

Salazar and Salazar (1999) have found numerous examples where bivalves have been the most sensitive test species. Their predicted tissue burden for effects in mussels is an order of magnitude lower than that for amphipods based on the work of Meador (1997 and references cited there in) and others. Theory suggests that tissue concentrations for effects should be relatively constant across species and that appears to be true for particular endpoints like growth. The problem is that it is relatively difficult to measure growth rate in an amphipod. The difference in sensitivity is due to the growth rate endpoint in bivalves and the mortality endpoint in amphipods which theory suggests is about an order of magnitude different (McCarty, 1991; McCarty and Mackay, 1993). An additional problem with most laboratory tests is that they were not originally selected and standardized by equilibrium kinetics and steady state.

Amphipod tests are routinely conducted for only 10 days, even though Meador (1997, 2000) has found that it takes about 45 days to reach chemical equilibrium or steady state. This may explain why there appears to

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be a disconnect between sediment chemistry, laboratory toxicity tests, and benthic community assemblages using the sediment quality triad. This has led to suggestions of using tissue chemistry to predict effects (McCarty, 1991; McCarty and Mackay, 1993). Subsequently Salazar and Salazar (1991; 1998; and Submitted) developed the exposure-dose-response triad that relies on tissue chemistry to make the link between the various effects endpoints. This relates to Salazar's point of growth rate affecting bioaccumulation potential. Sick and dying animals do not accumulate much TBT, which is why it is essential to confirm the health of the test animals.

With TBT data, they have been able to predict where effects will occur based on where the relationship between water or sediment and tissue TBT begins to change. This was first demonstrated in a graph published in Salazar and Salazar (1996) that plotted the relationship between water and tissue TBT. They found that grouping the data above 105 ng/L gave one regression and at 105 ng/L or lower that it gave a very different regression. The Salazar's recently replotted the Langston and Burt (1991) data and found exactly the same relationship, which Langston concurred. With Langston and Burt's data, they found effects in *Scrobicularia* to occur between 0.1 to 0.3 ug/g TBT dry weight in sediment, which agrees with Meador's data for effects on the polychaete *Armandia brevis* (Meador and Rice, In Press). The Salazar's summarized their findings in a paper presented at the SETAC (1999) meeting in Philadelphia. This paper is being expanded to emphasize the significance of field data over laboratory data in predicting effects and will be submitted to the Journal of Marine Environmental Research. They concluded that these data sets: (1) supports their hypothesis that one can predict the concentrations where effects will begin to occur based on the relationship between external concentrations and tissue burdens; (2) demonstrates that the concept may work for both water and tissue; and (3) suggests that tissue burdens associated with effects (acute 10X > chronic) are relatively constant across marine organisms.

ANTIFOULING BIOCIDES AND INVASIVE SPECIES

Recent research has suggested that hull biofouling will likely play a much greater role in introduction of invasive (exotic) species following a global ban on the use of TBT in antifouling paints. The 10[th] International Congress on Marine Corrosion and Fouling (February, 1999) in Melbourne Australia, included two special sessions on invasive species transported on vessel hulls. Stephan Gollasch, from the Institute for Marine Sciences in Germany gave a keynote address on the importance of ship hull fouling as a vector of species introductions into the North Sea. Dan Minchin presented a paper on data and information from Ireland and Mary Sue Brancato presented data from the U.S. (see also Brancato and MacLellan, 1999). Historically invasive species from the hulls of ships has been mostly an exotic marine algae and plants problem due to the speed and size of ships and water quality in ports.

Minchin estimated that 1.8 million marine organisms could exist on the hull of a severely biofouled vessel (Minchin, Personal Communication). However, after the introduction and use of TBT in the early 70's, fouling on hulls was not considered a significant source problem for invasive species, because in general hulls were cleaner. Considering the coincidence of global climate fluctuations and the proposed global ban on the use of TBT, invasion of species via the biofouling community on fouled hulls of ships may eventually constitute a greater threat then those in ballast water (Minchin and Sheehan, 1999).

Minchin is also concerned that there is a correlation between ship hull hitchhikers and water temperature changes. Ships pass through rapid water temperature fluctuations while entering harbors and channels and ports from the open ocean. These sudden temperature swings may initiate spawning triggering invasive species introduction in ports and port channels. Populations could easily become established in the invaded U.S. port because the U.S. Clean Water Act has greatly cleaned up (reduced pollution) U.S. ports over the years. In the past, the level of contamination in most ports has reduced the probability of the invading organism becoming established.. With the movement to clean up ports and harbors world wide, the risk of introduction has greatly increased. Minchin believes that IMO must have available replacements that are as effective as TBT, in providing the same degree of protection to coastal waters from invasive species as TBT has for the past three decades. To ban

it, we would face serious introduction of invasive species in the temperate environments. Their environmental impacts include changes in biodiversity, food webs, trophic levels competition, and the introduction of disease organisms and parasites.

It has been estimated that over 6000 species have been introduced in the U.S. The introduction of the lamprey eel and zebra mussel in the Great Lakes are examples of major invasive species. The zebra mussel has had detrimental effects on lakeside piers, industrial facilities and public beaches. Another example the European Green Crab (*Carcinus maenas*) has the potential to impact the $20 million dollar crab industry in the State of Washington alone (Brancato, 1999). Additional examples of invasive species are the Toxic Japanese dinoflagellates and the Northern Pacific sea star, which have infested New Zealand and Australia. The American comb jellyfish has greatly impacted the anchovy industry in the Black Sea.

In his keynote address at the 10th International Congress on marine Corrosion and Fouling, Stephan Gollasch reported on historical studies of invasive species in the North and Baltic Seas and compared vectors of introduction including ballast water and hull fouling from 200 ships. In the 1992 to 1995 time frame, Gollasch reported that most of the non-native species with the highest potential for establishment were from fouled hulls, with 53% of the marine exotic species found in the North Sea introduced by shipping and 98% of the hulls sampled revealed non-native species (Reise et al., 1999). Of the species connectable to shipping, 66% were introduced from the hull, 34% from ballast tanks. Gollasch, the second author of Reise et al. (1999) paper is also a scientific advisor and member of the German delegation for the ballast water working group at IMO's MEPC 43. He believes that IMO should consider the hull fouling dilemma in its assessment of the ban of TBT and balance the risk of introduction of invasive species harming local ecosystems with the environmental risks of TBT on non-target species in their decision-making process. He has found that most of the species of high concern are transported in ballast water including cholera bacteria and phytoplankton algae causing harmful algal blooms, but he believes the risk of species introduction

from ships hulls is increasing and without TBT it could be even worse (Gollasch, 1999, personnel communication).

TBT CONTAMINATION OF SEDIMENTS IN PORTS AND HARBORS

If TBT is banned by international treaty as proposed by MEPC 42, the future cost of removal of dredged material from harbors and waterways will probably increase significantly. An example of how regulation can increase disposal of dredged material costs is seen in the two alternatives available to the Port of NY/NJ for immediate disposal of dredge spoils. The Mud Dump Site (located 3 miles offshore in the open waters at the mouth of the harbor) has been operational for many decades and has been the traditional disposal area and can accept Category I dredged materials. Category II and III contaminated "spoils" have to be disposed of at an upland hazardous waste disposal facility, however, from 1977 to 1991, 90% of all NY/NJ dredge spoils were tested and classified Category I and only 1 to 2 % were Category III. However, in 1991 the US EPA replaced the existing tests in the NY region and added new bioassay testing which altered Category I, II, and III determinations.

For Category II and III dredged material, the currently available alternative is upland disposal at a hazardous materials storage facility and none are available in the near vicinity. Howland Hook Terminal in Staten Island shipped 150,000 yd^3 of sediment via barge and rail to Utah at a cost of $17 million or over $110/yd^3. Traditional fees for dumping dredge materials at the Mud Dump Site are in the area of $10/yd^3.

If TBT ("as perhaps the most toxic substance ever deliberately introduced to the marine environment by mankind") is banned by an international convention (it will be the first chemical by name to have its own convention or treaty) it could then be considered equal or more hazardous than Category III compounds. As such it might greatly increase the cost of disposal of dredged materials from most ports and harbors that are contaminated with TBT, because of its persistence and its universal distribution in bottom sediments of ports and ship channels.

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An additional concern for the paint companies, shipyards and shipping industry may be that in the future that they have bear the liability for cost contained dredging. It may be that the liability for the additional or special costs of dredging and disposal of TBT contaminated dredged materials from ports and ship channels might revert back in the courts to sources such as have the costs of health settlements from smoking in the courts. The impact on TBT contamination in port sediments on future shipping and port development is significant, for example, plans to dredge the Tyne in Newcastle (UK) may be abandoned, because of extremely high TBT concentrations in the river sediments, and the concern that organotins will desorb form particles on agitation during dredging and disposal of dredge material at sea (Mark G.J. Hartl, Personal Communication). Approval for dredging is pending on the outcome of a survey being conducted by CEFAS, Burnham On Crouch.

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Cost Analysis of TBT Self-Polishing Copolymer Paints and Tin-Free Alternatives For Use On Deep-Sea Vessels

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ABSTRACT

Despite the success of current restrictions on reducing tributyltin (TBT) and its environmental effects, a total ban on TBT for marine antifouling paints is gaining international momentum. The economic impacts of such a ban will be borne almost entirely by operators of deep-sea ships trading globally. These parties might be doubly affected if tin-free alternatives are found to be less effective in preventing fouling than TBT paints, and equally or more detrimental to the environment. We have conducted a comparative analysis of the costs of using TBT self-polishing copolymer (SPC) antifouling paints and their alternatives, to better understand the exact nature and sources of the economic impact on the operators of deep-sea vessels. This analysis included the costs of antifouling paint, dry-docking rates, clean hull fuel consumption, and fuel consumption penalties as a result of hull fouling.

Our analysis indicates that TBT SPC paints offer significant cost savings to shipowners and operators, because their five-year painting interval reduces dry-docking costs and revenues lost while the ship is in dry-dock. Tin-free antifouling paints cannot, at present, match the five-year painting interval TBT SPC paints can offer shipowners and operators. In a survey of shipping companies operating deep-sea vessels, we found that nine of eleven that use TBT paints operate on a five-year dry-docking and painting interval, whereas eight of eight that use tin-free paints dry-dock and paint on a 30-month cycle. The TBT painted ships operating on less than a five-year dry-docking interval generally did so because other maintenance needs necessitated more frequent dry-docking. Although tin-free SPCs require more frequent painting to maintain antifouling performance, their performance may be able to match TBT SPCs for the shorter painting interval (up to three years). Therefore, we have assumed no fuel penalty in comparing TBT SPCs and tin-free SPCs. Nonetheless, we found that tin-free SPCs are one to one-and-a-half times more expensive than TBT SPCs due to higher dry-docking costs, revenues lost, and paint costs. Furthermore, copper ablatives (as opposed to copper SPCs) are one-and-a-half to four times more expensive than TBT SPCs, due to fuel penalties, higher dry-docking costs, revenues lost, and paint costs. The ranges reflect the range of ship types and paint costs. The estimated annualized additional cost to the worldwide fleet of bulkers, container vessels, and very large crude carriers if a 30-month tin-free SPC is substituted for a 60-month TBT SPC is on the order of half a billion dollars. The penalty if a 30-month copper ablative coating were substituted for the 60-month TBT SPC is approximately $1 billion. These estimates incorporate the cost of coatings, dry docking costs, lost revenues, and a fuel penalty of four percent for copper ablatives. They do not include paint application costs, hull surface preparation costs, and waste disposal costs. They also assume no differences in fouling and hence no differences in fuel and other propulsion-related costs.

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INTRODUCTION

Despite the success of the current restrictions at reducing tributyltin (TBT) and its effects in the environment, a total ban on TBT for marine antifouling paints seems increasingly likely. It has been suggested in the literature (Hunter 1997a) that a ban would be a political decision, rather than one based on consideration of economic costs and environmental benefits. The economic impacts of such a ban will be borne almost entirely by operators of deep-sea ships trading globally (Pidgeon 1993). The affected parties might be doubly affected if tin-free alternatives are found to be less effective than TBT antifouling paints, and equally or more detrimental to the environment.

A comparative analysis of the costs (direct and indirect) of TBT antifouling paints and their alternatives is necessary in order to understand the exact nature as well as the sources of the economic impact on the operators of deep-sea vessels. This paper provides such a cost analysis for TBT antifouling paints as well as some of the current tin-free alternatives for deep-sea vessels.

The existing literature does contain several cost studies of TBT and tin-free alternative antifouling paints. These indicate specific cost implications, such as increased fuel costs of $50,000 to $400,000 per year, depending on vessel size (Burnett 1995), and losses in revenues, due to additional dry-docking, of $16,000 to $50,000 a day (Lloyd's Shipping Economist 1998, Vassalos and Stergiopoulos 1992). Few studies have examined all the cost factors related to a total ban on TBT-based antifouling paints. One such study (Milne 1996) uses TBT as a paradigm case of environmental cost-benefit analysis, concludes that using TBT results in a total savings per year of almost four billion dollars U.S., and examines the implications on greenhouse gas and acid rain issues. Another study examines the effects of a European Union (EU) ban on TBT-based antifouling paints on the different sectors including TBT manufacturers, paint manufacturers, ship repair yards, and shipowners and operators (WS Atkins 1998). Several articles reference the early CEFIC (1992) study that examined cost savings from using TBT-based self-polishing copolymer (SPC) paints. This study examined fuel savings and savings due to extended dry-docking intervals, and arrived at annual savings

of three billion dollars. A recent submission (Ichikawa 1998) to the International Maritime Organization's Marine Environmental Protection Committee (MEPC) from the Japanese Ministry of Transport also includes a cost analysis, but it appears to contain some important gaps and questionable assumptions. The Japanese study compares costs for a Panamax carrier for TBT and tin-free coatings. It does not clarify whether the tin-free, copper-based alternative is an SPC or ablative coating and it does not specify whether lost revenues due to additional dry-docking have been considered. Additionally, fuel penalties are assumed to be 3 percent, when the literature suggests this number varies from 2 to 10 percent. This is an important assumption because it affects the operating costs and therefore the profit margins of ship operators.

Our study extends previous cost analyses by examining the implications to three types of deep-sea vessels of switching from a TBT SPC antifouling paint to tin-free alternatives. We have obtained costs directly from paint manufacturers, shipyards, government agencies, and other sources. This study advances the literature by synthesizing these varied estimates into scenarios, refining estimates of additional costs that will occur because of imposed changes in TBT usage. We have attempted to be transparent about the data used, and the basis for all assumptions we made in performing the cost analysis.

Tributyltin has been used as an antifoulant in marine paints since its commercial introduction in 1965. Tributyltin antifouling paint technologies have changed considerably over that period (Bennett 1996). Early TBT antifouling paints were based on free association and insoluble matrix technologies. In free association paints, TBT was physically mixed into a soluble matrix. Dissolution of the matrix released the biocide into the water. In insoluble matrix coatings, the biocide was leached from the coating into the water. The biggest problem with free association and insoluble matrix antifouling paints was that their biocide release rate declined over time. This meant that the release rate on freshly painted hulls had to exceed levels required to prevent fouling, in order for the paint to remain effective for a reasonable period of time.

Modern TBT SPCs are copolymer systems. The surface layer of TBT copolymer coatings is hydrolyzed to

release TBT at a slow, uniform rate over the life of the paint. As the TBT is released, the surface layer becomes weakened and is eroded as the vessel moves through the water, continually exposing a smooth, fresh paint surface layer. Thus, the modern TBT coatings provide a controlled, uniform release rate and a self-polishing finish, which improves fuel efficiency. The TBT SPC technology also allows thicker paint coats, doubling the lifetime of the coating compared to previous technologies.

Modern TBT antifouling paints are currently used on over 70 percent of the world's ocean-going fleet (CEFIC 1996). Tributyltin antifouling paints are highly effective fouling inhibitors, and contribute substantially toward a ship's fuel consumption efficiency. Present TBT antifouling paints have in-service lengths of five years or longer, allowing some vessel owner/operators to extend dry-docking intervals and consequently reduce dry-docking expenses.

Elevated surface water concentrations of TBT have been observed where vessel usage was high, specifically in marinas and harbors (Hall et al. 1987, Langston et al. 1987). In the 1980s, concern about TBT's impacts on non-target organisms[1] became a policy issue, following the publication of Alzieu et al. (1981) linking shell deformations in the Pacific oyster (*Crassostrea gigas*) to TBT in antifouling paints.[2] Field and laboratory studies in the mid- to late-1980s documented a relationship between TBT concentrations in water and the formation of shallow cavities in the inner calcareous shell layer of *C. gigas* (Stephenson et al. 1986, Davies et al. 1988, Valkirs et al. 1987), a phenomenon known as chambering. These studies were conducted under exposure regimens with TBT concentrations (150 to 1,890 ng/L) many times higher than mean environmental concentrations reported recently (1992 - 1996) in waters of the U.S. (generally < 10 ng/L) (Russell et al. 1996).

Shell thickening attributed to TBT led to the decline of *C. gigas* shellfisheries in Arcachon Bay, France, and

resulted in France banning the application of all antifouling paints to the hulls of non-aluminum boats shorter than 25 meters.[3] The U.S. Congress passed the Organotin Antifouling Paint Control Act (OAPCA) in late 1988. This Act prohibited use of TBT-containing paints on ships under 25 m, with the exception of aluminum hulled vessels. It also limited TBT use to paints with laboratory-tested release rates not greater than 4 $\mu g/cm^2/day$. Similar restrictions were imposed in other nations. In most nations, the ban applies to vessels less than 25 meters in length, primarily affecting coastal vessels.

Legislation, where established, has been effective at controlling TBT levels in coastal environments. Monitoring data show reduction in TBT concentrations (Lange 1997, Batley 1996, Waite et al. 1991) and recovery of oyster fisheries (Stewart 1996). A critical review of current and future marine antifoulants was presented by the United Kingdom's delegation to the 35[th] session of the MEPC, held in March 1994 (Pidgeon 1993). MEPC 35 found that an extension of present TBT restrictions to a total ban was not justified on cost/benefit grounds, due to declining environmental risks and the absence of a satisfactory alternative to TBT. In the mean time, work on TBT alternatives has continued, particularly in Japan, where TBT antifouling paints are fully banned. A number of shipowners are painting their hulls with tin-free antifouling paints (Ichikawa 1998, Hunter 1997a). At least one paint company is now focusing its marketing efforts on the effectiveness of their tin-free antifouling paints (Hunter 1997b).

MATERIALS & METHODS

Our research yielded data sufficient to design and support a cost model using three ship classes widely found in the world fleet: a Panamax bulk carrier, a VLCC (Very Large Crude Carrier), and a container ship. The assumed characteristics of the three ships used in this study are based on ships in

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[1] Non-target organisms are those aquatic organisms not settling on ship hulls.
[2] The lethal and sublethal effects of TBT on marine life have been studied extensively since the early 1980s. Alzieu (1996) provides a review.
[3] Bosselmann (1996) provides a review of the history of environmental law concerning TBT in the environment.

current use. The steps in conducting the cost analysis include:

- identifying the alternative antifoulants;
- determining the dry-docking intervals for the different alternatives;
- determining the cost elements that are impacted by the alternatives;
- identifying data sources and collecting the data; and
- costing the alternatives.

Alternatives Considered

As a first step in the data collection process, we identified the range of commercially viable tin-free antifouling paints marketed for deep-sea vessels. These paints can be categorized by their chemical composition and mechanical properties. Tin-free ablative coatings are copper-based, and rely on physical processes to control the release of biocidal "boosters" mixed in the paint to increase antifouling effectiveness. The other primary category of tin-free alternatives are those based on SPC technologies; these encapsulate antifoulant boosters in chemical matrices similar in function to the SPC matrices found in modern organotin antifouling paints. These SPCs rely on chemical processes to release their antifoulants, providing a more uniform release rate over the life of the paint than copper ablatives. An additional benefit of SPCs is the self-polishing nature of the matrix. Properly applied, SPCs result in a nearly continuously smooth hull, reducing drag and associated bunker fuel consumption. Newer SPCs are based on copper acrylate and silicone functionalized methacrylate (silicone) technologies rather than organotin. This study does not include the silicone SPC, due to the reluctance of paint companies to provide the necessary cost data.

We have not examined paints containing naturally occurring antifouling compounds, or those that rely on low surface energy technologies. We concur with most observers that these paints either have not reached technological maturity or are poorly suited for use on the vast majority of hull types found in the world's deep-sea fleet. Low surface energy coatings are currently available and useful only for fast moving vessels such as some naval vessels, fast ferries and patrol boats. Since these coatings are not commercially available for all deep-sea vessels, this alternative is not considered in this study. Similarly, coatings with natural biocides are in developmental stages and therefore not considered here. Here we examine TBT SPC antifoulant coatings, and tin-free compositions that utilize either ablative or self-polishing mechanisms, and use a variety of biocide boosters.

Dry-Docking Intervals

We found no data indicating that tin-free antifouling paints can, at present, match the 60-month dry-docking interval TBT SPC paints can offer shipowners and operators. However, at least one paint company claims that alternative paints match the performance of their TBT SPC competitors at intervals of up to 36 months. The data we have obtained indicate that a paint's performance is highly variable (based not only on physical application but also in-service maintenance, routes, operating profiles, etc.). Ships that are on a shorter dry-docking cycle appear to dry-dock every 32 months on average (Hunter 1997b). The recent submission to the International Maritime Organization by the Japanese Ministry of Transport (Ichikawa 1998) uses a 30-month dry-docking interval. The literature suggests that vessels might be dry-docking anywhere between 27 months and 60 month intervals (Aubert 1998, Hunter 1997a), and paint companies claim efficacies for 36 month and 60 month intervals (Hunter 1997b). The literature indicates that the 60-month interval is proven for TBT SPC coatings, whereas the non-TBT SPCs and the copper ablatives are effective for a maximum of 36 months (Hunter 1997a).

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To verify some of this information, we conducted telephone and mail surveys of shipowners worldwide, and contacted Lloyd's Maritime Information Services (LMIS) for dry-docking information. The survey results showed that nine of eleven shipping companies that use TBT paints operate on a five-year dry-docking interval, whereas eight of eight that use tin-free paints dry-dock on a 30-month cycle. The TBT painted ships operating on less than a five-year dry-docking interval generally did so because other maintenance needs necessitated more frequent dry-docking. In-water survey information obtained from LMIS for 76 ship types with average lengths greater than 50m were reviewed. Vessels for which in-water surveys are conducted are likely on five-year dry-docking cycles rather than 30-month cycles. The LMIS data support our assumption of a five-year painting interval for TBT-painted ships.

In light of the data we have obtained, there appears to be a five-year dry-docking interval for TBT SPC-painted vessels. As a result, our analysis used a 60-month dry-docking interval for TBT SPCs and a 30-month dry-docking interval for tin-free coatings.[4]

Cost Elements

As often voiced in submissions to the MEPC and in the trades press, the debate surrounding any ban on the use of organotin-containing antifoulants centers on the issue of cost. Examination of previous cost analyses (Ichikawa 1998, Milne 1996) provided two analyses with radically different aims and outcomes. With limited guidance to draw from these studies, we undertook a regimen of questioning industry insiders to

ascertain the types of data required for determining the costs of applying one antifouling paint versus another. These inquiries yielded the following relevant cost elements, upon which our cost model is built:

- antifouling paint costs,
- dry-docking rates,
- clean hull fuel consumption, and
- fuel consumption penalties as a result of hull fouling.

Modeling assumptions are discussed in a following section.

Data Collection Methodology

We relied heavily on personal interviews with industry representatives and a thorough literature review. Individuals representing paint manufacturers, shipyards, shipping companies, the United States Navy, the U.S. Department of Transportation Maritime Administration (MARAD), LMIS, and maritime trade associations, among others, were contacted and asked to provide insights and data to populate the cost model. Surveys were developed to obtain information from paint manufacturers, shipping companies, and shipyards worldwide (Damodaran et al. 1998). The literature review was conducted in the libraries of the International Maritime Organization in London and the Department of Transportation library in Washington, D.C. It included a thorough examination of trade publications, publicly available reference materials, specialized reports on segments of the maritime industry, and government publications and reports. Data on ship dry-docking schedules and ship condition surveys were obtained in a database format from LMIS.

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[4] U.S. ships are required by law to dry-dock every 30 months. The U.S. Maritime Administration (MARAD 1997) reports that of the world's 26,764 ocean-going merchant ships (greater than or equal to 1,000 gross tons), 498 (1.86 percent) are U.S. ships.

RESULTS & DISCUSSION

As discussed in the methodology section above, we utilized a two-pronged approach of primary and secondary (i.e., literature review) data collection. Our primary data collection included discussions with government agencies, associations, and industry contacts. Government agencies, particularly MARAD, provided statistics on the shipping industry and world fleet. In addition, several individuals at MARAD provided insight regarding dry-docking procedures in general, and in particular with regard to the application of antifouling paints. The various associations we contacted provided little more than anecdotal information.

Our efforts to collect data from industry sources included contacting coatings manufacturers, ship repair yards (dockyards), ship maintenance subcontractors, and shipping companies/shipowners. The five paint companies that account for 80 percent of the market share were contacted for information on paint costs. Three companies that account for over 60 percent of the market share responded with useful data. Nine shipyards were contacted, with three providing useful information.

Four of the five contacts made in shipping information companies resulted in data and studies on shipping statistics. Of the eleven shipping owners and operators, only one responded with information associated with conversion from TBT to tin-free antifouling paints. It should be emphasized that time constraints prevented us from following up on these contacts, or making additional contacts in this sector.

We have expressed all costs in 1997 U.S. dollars, and estimated costs for a container, a bulk carrier and a VLCC, which represent three major classes of deep-sea vessels. It was assumed that the life of a ship is 25 years and all costs are calculated over the life of the ship.

Paint Costs

The first category of costs examined was paint costs associated with the three types of ships. Paint costs were calculated based on information received from three paint companies. The paint companies typically provided unit costs as well as quantities required for the three types of vessels.

They were asked to quote prices for antifouling systems for the three representative ships (one container ship, one Panamax bulk carrier, and one VLCC). Paint costs from two paint companies were obtained in this manner. A third company quoted price ranges for three popular product lines, as well as providing estimated paint volumes required to paint 10,000 m². When asked about painting a larger hull area, this company suggested we "ramp up" from the given figure, which is what we have done. Because paint costs vary, we examined the overall costs based on both the minimum and the maximum paint cost associated with the different paint categories, as shown in Table 1.

Table 1. Minimum and maximum paint costs over a 25 year life (1997 US $).

Ship type and paint costs	TBT SPC (60 months)	Copper SPC (30 months)	Copper ablative (30 months)
Container – minimum	644,086	1,040,346	438,649
Container – maximum	733,104	1,377,180	1,368,995
Bulk carrier – minimum	308,178	835,934	223,694
Bulk carrier – maximum	642,308	1,052,834	717,447
VLCC – minimum	647,267	1,903,852	601,183
VLCC – maximum	722,732	2,022,378	2,093,503

VLCC = Very large crude carrier

When compared, it is clear that TBT SPCs are substantially less expensive than copper SPCs. Copper SPC paint costs vary from being 62 percent more expensive using the minimum cost paints for the container ship, to 194 percent more expensive for the VLCC using the minimum cost paints. Although the container ship is closer to a bulker in size, paint manufacturers have typically indicated that container ships require more paint per square meter than the bulkers or the VLCCs. The faster speeds of these ships may be one reason for the increased quantities required.

The costs of paint application, including surface preparation, labor, and waste disposal, are necessary for a more complete picture of the costs. These costs, while likely a significant component in the decision to apply a given antifouling paint, are discounted in this study for several reasons.

Waste disposal costs are likely to be greatly impacted by the level of environmental regulation present in any given nation. The variability of the enforcement of these regulations, and the subsequent variations in waste disposal costs, make it very difficult to estimate these highly variable costs. Regarding hull surface preparation and application costs, the study team was hindered by the competitive nature of the ship repair industry, and individual yard's reticence to release proprietary information. Even market specialists such as Lloyds' Shipping Economist and Drewry's are unable to estimate or ascertain these costs.

While it is possible to overcome these obstacles and obtain the data, it was beyond the scope of this study to pursue this information.

Dry-Docking Costs

Dry-docking rates were obtained from one Japanese interest; these were confirmed as realistic, through comparison with figures in the literature, and incorporated into the cost model. A review of the literature indicated that the number of days in dry-dock varied from estimates of four (and Stergiopoulos 1992) to 20 days (Kawai 1998) depending on the ship type and other factors such as required maintenance. This study assumes the lower end of the range for each of our ship types, as provided by the Japanese shipyard that provided dry-docking rates as well. The number of dry-docking days is assumed to be seven days for the bulk carrier and container ships, and 14 days for the VLCC. The rates were dependent on the gross tonnage of vessels and daily rates were calculated to be $7,185 for the bulk carrier, $9,786 for the container ship and $14,424 for the VLCC.

Lost Revenue

The operators of the vessels experience a loss in revenue for every day that the ship is in dry-dock as opposed to being in operation. These daily revenues were estimated from the literature (Lloyd's Shipping Economist 1998). For the bulk carrier, the daily revenues were estimated to be $16,000. Daily revenues for the container vessel and VLCC were $19,175 and $12,500, respectively.

Fuel Penalty

Tributyltin SPCs are widely considered the most effective commercially available antifoulants. Empirical evidence (Hunter 1997b) indicates that 96 percent of ships with TBT SPC coatings come to port in the 30 to 36 month dry-docking interval with satisfactory performance. The equivalent numbers for tin-free SPCs are 90 percent and about 70 percent for copper ablatives. The less effective an antifoulant, the more hull drag increases fuel consumption and fuel consumption costs. In the process of evaluating competing performance claims, we have relied heavily on industry and trades sources. International Paints claims its Ecoloflex tin-free SPC displays similar performance characteristics to its TBT SPC product line. Without access to proprietary data regarding same-ship performance, we are unable

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to either confirm or refute this claim. Thus, we assume International Paint's performance claims vis-à-vis the Ecoloflex product line to be accurate. Fuel penalties associated with the use of copper ablatives vary from two to 10 percent with 4 percent being most frequently cited. This study uses 4 percent as a fuel penalty for comparing costs across the categories of antifoulants. It also compares the copper ablatives to the 60-month TBT SPC system using a range of fuel penalty rates.

Costing the Alternatives

The costs of the alternatives were calculated for the three representative ships: a Panamax bulk carrier, a container ship, and a VLCC. The life of the vessels was assumed to be 25 years. The paint costs, dry-docking costs, lost revenues, and fuel penalties were calculated over the life of the vessels. The number of dry-dockings was estimated to be four using a 60-month TBT SPC system. The number of dry-dockings is nine using a 30-month interval for the copper SPC and the copper ablative systems. It should be noted that fuel penalties were calculated only for the ablative coatings. Because we used both the minimum and maximum paint costs, the comparative analysis was conducted for both costs for all three vessel types. In all cases the 60-month TBT SPC was used as a baseline against which the other systems were compared. The detailed tabular breakdown of costs is presented in Damodaran et al. (1998).

Figures 1 and 2 show the costs for the bulk carrier using maximum and minimum paint costs. The copper SPC system costs 95 percent more than the 60-month TBT system using the maximum paint costs and is 140 percent more expensive when using the minimum paint costs. The ablatives are much more expensive; using the maximum paint costs for a 60-month TBT SPC system results in a 156 percent cost increase, and using the minimum paint costs results in a 193 percent cost increase.

Figures 3 and 4 show the costs for the container ship using maximum and minimum paint costs. The copper SPC system cost 107 percent more than the 60-month TBT system using the maximum paint costs and is 97 percent more expensive when using the minimum paint costs. The ablatives are much more expensive; the maximum paint costs result in a 401 percent increase and the minimum paint costs result in a 368 percent increase over using a 60-month TBT SPC system.

Figures 5 and 6 show the costs for the VLCC using maximum and minimum paint costs. The copper SPC system cost 143 percent more than the 60-month TBT system using the maximum paint costs and is roughly equivalent at 146 percent more expensive when using the minimum paint costs. Again, the ablatives are much more expensive. Using the maximum paint costs for a 60-month TBT SPC system results in a 250 percent cost increase and using the minimum paint costs results in a 193 percent increase.

Sensitivity Analysis of Fuel Penalties

Numerous studies claim various "penalties" with regard to fuel consumption for ships that use copper ablative antifoulants as opposed to TBT SPC coatings. In our study, we have assumed a 4 percent fuel penalty, based on the 1992 IMO paper presented by CEFIC. In order to examine the importance the assumed fuel penalty plays in determining total costs of using ablatives instead of SPC coatings, we have graphed (Figures 7 and 8) the total costs given fuel penalties ranging from 2 to 10 percent for both maximum and minimum paint cost assumptions. In the case of the VLCC, a fuel penalty of 10 percent almost doubles the total costs relative to a 2 percent penalty. For a bulker ship, a doubling is apparent. For the container ship, there is a tripling in costs when these fuel penalty extremes are considered. Container ships are particularly sensitive to fuel penalties because they run at faster speeds than

bulkers and crude carriers. It is important to note that the total costs shown here do not represent all the operating costs that must be considered; for example, labor cost at dockyards, surface preparation of the hulls, and waste disposal costs are not considered in this analysis. Including these further increases the costs of tin-free alternative antifouling coatings.

Based on our review of the literature, our estimates of fuel consumption differences as a function of antifoulant type seem reasonable. For example, in our study, a hypothetical VLCC painted with a copper ablative coating requires $92,000/year

more for fuel than if it was coated with an SPC. Lanz (1995) considered a larger tanker, and estimated that this difference is $100,000 annually. A ship with moderate green weed fouling typically consumes 10 percent more fuel than a similar vessel with a smooth hull. For a 40,000 dead weight tonnage (dwt) bulk carrier this would result in an extra $72,000 in fuel bills per year (based on $100/ton fuel costs, 30 tons/day and 240 days at sea). Under a 10 percent fuel penalty assumption, fuel costs for our larger bulk carrier (54,000 dwt) would be $112,000. Table 2 shows the increased costs associated with a variety of fuel penalty rates.

FIGURE 1

	PAINT COST	DRYDOCK COSTS	LOST REVENUES	FUEL PENALTY
TBT SPC	$642,308	$201,170	$448,000	
COPPER SPC	$1,052,834	$452,633	$1,008,000	
COPPER ABLATIVE	$717,447	$452,633	$1,008,000	$1,124,565

FIGURE 2

	TBT SPC	COPPER SPC	COPPER ABLATIVE	
PAINT COST	$308,178	$835,934	$223,694	
DRYDOCK COSTS	$201,170	$452,633	$452,633	
LOST REVENUES	$448,000	$1,008,000	$1,008,000	
FUEL PENALTY				$1,124,565

FIGURE 3

	TBT SPC	COPPER SPC	COPPER ABLATIVE	
PAINT COST	$733,104	$1,377,180	$1,368,995	
DRYDOCK COSTS	$274,021	$616,547	$616,547	
LOST REVENUES	$536,900	$1,208,025	$1,208,025	
FUEL PENALTY				$4,548,960

FIGURE 4

	TBT SPC	COPPER SPC	COPPER ABLATIVE	
PAINT COST	$644,086	$1,040,346	$438,649	
DRYDOCK COSTS	$274,021	$616,547	$616,547	
LOST REVENUES	$536,900	$1,208,025	$1,208,025	
FUEL PENALTY				$4,548,960

FIGURE 5

	TBT SPC	COPPER SPC	COPPER ABLATIVE	
PAINT COST	$722,732	$2,022,378	$2,093,503	
DRYDOCK COSTS	$807,737	$1,817,409	$1,817,409	
LOST REVENUES	$700,000	$1,575,000	$1,575,000	
FUEL PENALTY				$2,324,205

FIGURE 6

	TBT SPC	COPPER SPC	COPPER ABLATIVE	
PAINT COST	$647,267	$1,903,852	$601,183	
DRYDOCK COSTS	$807,737	$1,817,409	$1,817,409	
LOST REVENUES	$700,000	$1,575,000	$1,575,000	
FUEL PENALTY				$2,324,205

FIGURE 7(MAX)

BULKER	CONTAINER	VLCC
$2,740,363	$5,468,047	$6,648,015
$3,021,504	$6,605,287	$7,229,066
$3,302,645	$7,742,527	$7,810,118
$3,583,786	$8,879,767	$8,391,169
$4,146,069	$11,154,247	$9,553,271
10$4,989,493	$14,565,967	$11,296,425

FIGURE 8 (MIN)

BULKER	CONTAINER	VLCC
$2,246,610	$4,537,701	$5,155,694
$2,527,751	$5,674,941	$5,736,746
$2,808,892	$6,812,181	$6,317,797
$3,090,033	$7,949,421	$6,898,848
$3,652,316	$10,223,901	$8,060,951
10$4,495,740	$13,635,621	$9,804,104

PANAMAX BULK CARRIER (BASED ON MAXIMUM PAINTS COSTS)

FIGURE 1.
ESTIMATED LIFETIME COSTS FOR A SINGLE   PANAMAX BULK CARRIER, ASSUMING MAXIMUM PAINT COSTS.

PANAMAX BULK CARRIER (BASED ON MINIMUM PAINTS COSTS)

FIGURE 2.
ESTIMATED LIFETIME COSTS FOR A SINGLE   PANAMAX BULK CARRIER, ASSUMING MINIMUM PAINT COSTS.

CONTAINER SHIP (BASED ON MAXIMUM PAINT COSTS)

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Table 2. Cost comparison of copper ablative and TBT SPC as a function of fuel penalty (percentage increase over the costs of a 60-month TBT SPC).

% Penalty	Fuel	Bulker		Container		VLCC	
		Max	Min	Max	Min	Max	Min
2		112	135	254	212	198	139
3		134	164	328	290	224	166
4		156	193	401	368	250	193
5		177	223	475	446	276	220
7		221	282	622	603	328	274
10		286	370	843	837	406	355

Costs to the Worldwide Deep-Sea Shipping Fleet

In addition to calculating costs for individual vessels, we have estimated the costs to the world fleet of bulkers, container vessels, and VLCCs, which together comprise 75 percent of the world fleet deadweight tonnage. Our estimates incorporate the cost of coatings, dry-docking costs, lost revenues, and a fuel penalty of 4 percent. They do not include paint application costs, hull surface preparation costs and waste disposal costs. Maximum and minimum paint costs bound the range of antifouling coating costs quoted by manufacturers. The differential highlights the difference between the TBT SPC and its alternatives. The cost difference between the copper SPC system and the TBT SPC is approximately $500 million (Table 3), and that for the copper ablative system versus the TBT SPC approximately $1 billion (Table 4). These cost difference estimates probably are biased low because the tin-free paints require more frequent dry-docking, and therefore, are expected to have higher paint application, hull preparation, and waste disposal costs.

Table 3. Estimates of the costs of using a 30-month copper SPC antifouling system relative to a 60-month TBT SPC system on bulker, container and VLCC ships worldwide.

Ship Type	Annual Lifecycle Cost Differential ($)[a]	Dead-Weight Tonnage	$/Dead Weight Ton[a]	Millions of Dead Weight Tons (Worldwide)	Financial Impact on World Fleet[a]
Bulker[b]	48,880/53,569	54,500	0.90/0.98	239.2	214.5/235.1
Container	66,309/56,396	30,825	2.15/1.83	48.6	104.5/88.9
VLCC	127,373/125,650	137,684	0.93/0.91	270.3	250.1/246.7
Total	-		-	-	569.1/570.7

[a] Based on maximum/minimum paint costs.

[b] The bulker's annual lifecycle cost differential is higher for the minimum coatings cost than for the maximum coatings cost because the difference between the minimum copper SPC and TBT SPC paint costs is greater than the difference between the maximum copper SPC and TBT SPC paint costs.

Table 4. Estimates of the costs of using a 30-month copper ablative antifouling system relative to a 60-month TBT SPC system on bulker, container and VLCC ships worldwide.

Ship Type	Annual Lifecycle Cost Differential[a]	Dead-Weight Tonnage	$/Dead Weight Ton[a]	Millions of Dead Weight Tons (Worldwide)	Financial Impact on World Fleet[a]
Bulker	80,447/74,062	54,500	1.48/1.36	239.2	353.1/325.1
Container	247,940/214,287	30,825	8.04/6.95	48.6	390.9/337.9
VLCC	223,186/166,512	137,684	1.62/1.21	270.3	438.2/326.9
Total	-		-	-	1,182.1/989.8

[a] Based on maximum/minimum paint costs.

CONCLUSIONS AND RECOMMENDATIONS

We have undertaken a comparative analysis of the costs (direct and indirect) of TBT SPC antifouling paints and their alternatives, in order to understand the nature and sources of the economic impact on the operators of deep-sea vessels. Additionally, we have examined what is known about the environmental fate and effects of tin-free alternative antifouling paints. We have drawn five general conclusions, presented below.

1. Tributyltin SPC paints offer significant cost savings to shipowners and operators because their five-year dry-docking interval reduces dry-docking costs and revenues lost while the ship is in dry-dock for cleaning and repainting. We found no data indicating that tin-free antifouling paints can, at present, match the five-year dry-docking interval TBT SPC paints can offer shipowners and operators.

2. There are claims that alternative paints match the performance of their TBT SPC competitors at intervals of up to three years. Therefore, we have assumed no fuel penalty in comparing TBT SPCs and copper SPCs. Nonetheless, we found the copper SPCs are 95 - 146 percent more expensive than the TBT SPC due to higher dry-docking costs, revenues lost, and paint costs. Copper ablatives were 156 percent - 401 percent more expensive than TBT SPCs, due to fuel penalties, higher dry-docking costs, revenues lost, and paint costs. The ranges reflect the range of ship types considered in the analysis and uncertainty about paint costs.

3. The estimated penalty to the worldwide fleet of bulkers, container vessels, and VLCCs when copper SPC is substituted for a TBT SPC is on the order of $500 million. When a copper ablative coating is substituted for the TBT SPC, the penalty is approximately $1 billion. These estimates incorporate the cost of coatings, dry docking costs, lost revenues, and a fuel penalty of 4 percent for the copper ablative paint. They do not include paint application costs, hull surface preparation costs and waste disposal costs, and these costs would approximately double for the shorter dry-docking interval. The literature indicates that the fuel penalty for copper ablatives may be as high as 10 percent, in which case the $1 billion annual cost differential would be an underestimate.

4. We have qualitatively assessed the effect of a worldwide TBT ban on five different sectors: tributyltin oxide (TBTO) producers, paint companies, dry docks/repair yards, shipowners/operators, and the environment. Our results indicate paint companies are positioned to capture a windfall if TBT is banned, and that owners/operators, and ultimately consumers, stand to lose. The impact on dry docks/repair yards would depend on how a TBT ban was enforced; if enforcement is uniform it could mean a windfall, if not it could simply mean work shifting to locations where enforcement is lax.

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5. The final sector in our analysis is the environment. The data we have acquired indicate that TBT and copper SPCs provide the same fuel efficiency, so the environmental risks or benefits of switching from a TBT SPC to a copper SPC would have to do primarily with the pesticidal impacts on non-target organisms. We have not found extant data or analyses sufficient to quantitatively compare the risks of tin-free antifouling paints to TBT. Critical data gaps include chronic toxicity data for biocide boosters, and estimates of environmental concentrations for some of the boosters. However, the data on SeaNine-211 and Irgarol 1051 indicate that paints containing either of these biocides do pose risks to the environment. Based on the data currently available on TBT and tin-free antifouling paints, none of the tin-free alternative antifouling paints have been shown to be as safe as or safer for the environment than TBT SPC paints, for use on deep-sea vessels.

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Aquatic Ecological Risks Posed By Tributyltin in U.S. Surface Waters: PRE-1989-1996 Data[1]

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ABSTRACT

Acute and chronic risks to aquatic life from exposure to tributyltin (TBT) in surface waters were assessed probabilistically using more than nine years of monitoring data. More than 50 sites around the United States were sampled, representing six saltwater regions and one freshwater (Lake Erie). Ambient TBT concentrations were compared to acute and chronic effect thresholds to estimate risks for each year (1986 - 1988, 1992 - 1996), site type, and region. Site types comprised commercial harbors, shipyards, marinas, and fish/shellfish habitats proximate to these commercial areas.

Tributyltin concentrations in surface waters have declined in all regions and site types since passage of the Organotin Antifouling Paint Control Act in 1988. No risks of acute toxicity have been suggested since 1994. Chronic risks have remained highest in marinas compared to other site types, but have declined from a risk involving 25 percent of the species prior to 1989 to one involving 6 percent of the species in 1996. Risks associated with commercial harbors and shipyards have been similar (4 - 6%) since 1994. Chronic risks have been ≤ 1 percent in fish and shellfish habitats sampled < 1 - 2 km from TBT sources. Risks in Galveston Bay, over all years, (1 - 19%) have been greater than in the other regions (≤ 5%).

INTRODUCTION

Tributyltin (TBT) has been used as an antifoulant in marine paints since its commercial introduction in 1965 [1, 2]. Elevated surface water concentrations of TBT have been observed where vessel usage was high, specifically in marinas and harbors [3, 4]. Tributyltin exerts chronic effects on aquatic organisms at concentrations down to ±10 - 20 ng/L, and 10 ng/L has been proposed by the U.S. EPA as the chronic marine water quality criterion protective of at least 95 percent of aquatic organisms [5]. In the 1980s, concern about risks to non-target organisms prompted passage of the Organotin Antifouling Paint Control Act (OAPCA) by the U.S. Congress in late 1988. This Act restricted use of TBT-containing paints to ships over 25 m and those with aluminum hulls. It also limited TBT use to paints with laboratory-tested release rates of ≤ 4 μg/cm^2/day. Subsequent to restrictions on TBT usage, environmental monitoring revealed declining TBT concentrations in the U.S., Europe, and Japan [1, 6-10]. For instance, since passage of OAPCA, median TBT concentrations in U.S. marine waters generally have averaged less than 10 ng/L, the EPA [5] chronic marine water quality criterion [11]. Concentrations in the freshwater region monitored (Lake Erie) have been less than EPA's freshwater chronic water quality criterion, 63 ng/L, since 1991 [11].

The objective of this study was: 1) to determine acute and chronic risks to aquatic life from exposure to TBT in U.S. surface waters, and 2) to evaluate regional and source-related (e.g., marinas, commercial harbors, shipyards) differences in risks. Risks in saltwater were emphasized because fouling on boat hulls is generally higher in saltwater versus freshwater, therefore TBT use is higher on saltwater vessels. The risk assessment approach used is probabilistic because it models variability in estimated TBT exposure levels as well as in TBT's acute and chronic toxicity to aquatic organisms.

RISK CHARACTERIZATION METHODS

Acute and chronic risks were estimated by comparing distributions for TBT EECs and effects thresholds. The estimated risk for any given EEC equals the percentage of taxa affected at that EEC. The probability associated with this level of risk is the probability that the stated EEC will occur. For the entire distribution of TBT concentrations (R(EEC)), the percentage of taxa expected to be at risk is plotted against (f(EEC)), the probability associated with the EEC. This creates the risk PDF. Expected total risk is found by summing (or integrating) the product R(EEC)*f(EEC). Expected total risk can also be considered a weighted average where risks associated with a given EEC are weighted by the probability of occurrence. Table 1 exemplifies the probabilistic risk estimation method. For example, a TBT concentration range of 0 - 5 ng/L encompasses 47 percent of the EECs, and within the 0 - 5 ng/L range only 0.041 percent of the taxa will be affected. The percent taxa at risk is 47% x 0.041% = 0.019%. The statistical expectation of the risk is simply the sum (or integral in the continuous case) of the possible risk levels, each weighted by its probability of occurrence.

RISK CHARACTERIZATION RESULTS

The risk characterization presents the results of the probabilistic risk analysis with the percentages of taxa expected to be at acute or chronic risk of exposure to TBT concentrations in the water column. First, we discuss the risks of acute and chronic toxicity on a regional basis. This is followed by a discussion of the risks associated with the different sources of TBT; a discussion of the results that would be obtained from a hazard quotient approach versus the approach applied herein; and last, the ecological significance of the risks and uncertainties.

Risks posed to aquatic life by TBT concentrations in U.S. surface waters have varied significantly between regions of the U.S. and the sites monitored (Tables 2a-e). At most of the sites and regions monitored, risks were low, affecting ≤ 6 percent of the species even prior to OAPCA's passage in 1988. These risks seem lower than those based on comparing a specific TBT effect criterion (e.g., 10 ng/L) to a specific EEC value or frequency (e.g., 36% of EECs exceeded the criterion). By taking a community-based approach and considering the relative sensitivity of species within that community, expected total risk (ETR) turns out to be less. Because TBT water column concentrations continued to decline over time, the majority of the characterization focuses on the ETRs calculated for 1996 because they represent the most recent data collected.

Risks of Acute Toxicity

Risks of acute toxicity have been low (≤ 3%) since prior to OAPCA because TBT's acute toxicity occurs at ≥ 110 ng/L. EPA [5] has estimated the acute toxicity threshold at ≥ 356 ng/L. By 1993, there was no risk of acute toxicity in Puget Sound, Lake Erie, or Narragansett Bay. Acute risks occurred only within Galveston Bay's commercial sites, and by 1996, ≤ 1 percent of the aquatic taxa were at risk to acute toxicity at these sites.

Regional Differences in Chronic Risks

Tributyltin concentrations typifying each of the site types differed between regions, with chronic risks being higher (12 to 14% in 1996) in Galveston Bay and negligible (≤ 4%) in the other regions (Tables 2a-d). The ETR for Puget Sound and Narragansett Bay in 1996 was ≤ 3 percent at all site types. In Lake Erie, risks were < 1 percent except at marinas (≤ 2%). In Galveston Bay, ETRs were 12 to 14 percent at all site types except fish/shellfish habitats (≤ 1%). The regional differences in risks reflect the higher EECs seen in Galveston Bay (Tables 2a-d). Leading explanations concerning Galveston Bay's elevated TBT

concentrations include greater shipping activity and naturally elevated suspended solids (8 to 155 mg/L) which offers a substrate for TBT sorption [34].

Source Differences in Chronic Risks

Expected chronic risk also varied greatly by site type (Table 2a). Over the nine plus years of monitoring (the Navy and EPA programs), ETRs have been highest in marinas (5 to 25%), followed by shipyards (5 to 6%), commercial harbors (< 1-6%), and fish and shellfish habitats proximate to these sites (< 1-2%). While this reflects differences in exposure (i.e., differences in EEC distributions), different organisms also inhabit the various site types. The latter is not a factor in the risk estimates, which assume a diverse saltwater community is attainable in commercial sites.

The site type differences were also reviewed at the regional level using 1992 - 1996 data (Tables 2b-e). The pattern was similar for Puget Sound, Narragansett Bay, and Lake Erie, where ETRs were highest in marinas (2 to 9%), low in commercial harbors and shipyards (< 1 to 5%), and even lower in fish and shellfish habitats (< 1 to 2%). While a similar pattern was seen in Galveston Bay, ETRs were higher (Table 2b). In Galveston Bay, ETRs in marinas were highest (13 to 19%), followed by shipyards (12 to 15%), commercial harbors (8 to 14%), and fish and shellfish habitats (1 to 4%).

Trends in Chronic Risks

Annual monitoring of each TBT site type from pre-OAPCA to 1996 reveals ETRs decreasing over time in saltwater marinas, the only site type where risks were high enough to track temporal trends (Table 2a). Prior to 1989, ETRs were as high as 25 percent in saltwater marinas; but by 1996, they had declined to ≤ 14 percent in Galveston Bay at all four site types, and to ≤ 2 percent in all Puget Sound and Narragansett Bay site types except marinas (3 - 4%) (Tables 2a-e). Risks at the Lake Erie sites have remained low (0 - 2%) since monitoring commenced in 1992. To place these risks into context, the EPA water quality criteria seek to protect all but 5 percent of the species, and the Society of Environmental Toxicology and Chemistry [25] recommends protecting all but 10 percent of the species. Economically important species and those that

influence the community out of proportion to their abundance or biomass (keystone species) also are protected.

Comparison of Risk Characterization Approaches

Risk assessments often are conducted in tiers (phases), with a screening phase based on quotients usually conducted in Tier 1 and a detailed phase based on probabilistic techniques conducted in Tier 2. Risks suggested by the two approaches may appear quite different, reflecting dissimilar assumptions and calculation methods. With the quotient method, risks appear higher because the probabilities of exposure and effect are not considered; a quotient only compares the magnitude of the ratio between the EEC and the toxicological effect threshold. In 1996, for example, 40 percent of the EECs measured in U.S. saltwater marinas and 3 percent of those in proximate fish and wildlife habitats exceeded the EPA chronic criterion of 10 ng/L, the former suggesting substantial risk. However, the WERF methodology [12] indicates the ETR to be ≤ 6 percent of all saltwater species in marinas and ≤ 1 percent in ecological sites. That is, on average, only < 1 - 6 percent of the taxa are predicted to be at risk of chronic toxicity in the sites and regions sampled (Table 2a).

The measure of risk used in the WERF methodology is the percentage of aquatic taxa whose effects thresholds are exceeded by the EECs to which they are exposed. Using marinas as an example, 24 percent of all EECs measured in saltwater marinas in 1996 exceeded 16 ng/L. At the latter EEC, approximately 10 percent of the saltwater taxa are expected to be at risk of chronic toxicity, i.e., to incur adverse effects on some proportion of their population given the assumptions made concerning duration and bioavailability of TBT exposure. Consequently, the ETR is 2.4 percent (24% x 10%).

The most sensitive 10 percent of taxa tested include larvae of certain bivalves (e.g., *Mercenaria, Crassostrea*), gastropods (e.g., the snail *Nucella*), and crustacea (e.g., the copepod *Acartia*) [5]. For example, a percentage of the quahog clam's (*Mercenaria mercenaria*) larvae are at risk when chronically exposed to 10 ng/L TBT at the veliger stage; chronic effects have been observed at 10 ng/L [5]. Because EECs in

the range of ≥ 10 ng/L occurred in 1996 40 percent of the time in marinas, it can be assumed they occurred over sufficiently long time periods to encompass bivalve larval development (~ 21 days). In 1996, risks to quahog clam larvae occurred in Galveston Bay's commercial sites; risks in the other regions were lower, as discussed below.

Ecological Significance of the Chronic Risks

Concentrations > 10 ng/L may have occurred long enough to pose chronic risk to species with short life cycles or sensitive life stages, such as developing bivalve larvae and reproduction of copepods like *Acartia tonsa* [35]. Despite the ETRs to certain species sensitive to TBT, it is not clear how chronic effects at early life history stages would affect populations as a whole. For example, a variety of indigenous bivalve species whose larvae are expected to be as sensitive to TBT as those tested in the laboratory have been collected in all of the saltwater regions monitored. The primary bivalves collected include *Mytilus trossulus* in Puget Sound, *M. edulis* and *Arcuatula demissus* in Narragansett Bay, *Crassostrea virginica* in Galveston Bay, and *Dreissena polymorpha* in Lake Erie. In Galveston Bay, where TBT concentrations were higher, bivalve populations were not as large or as frequent at some of the monitoring sites, yet it is clear that exposure is either less than predicted or that compensatory mechanisms at later life history stages may offset reductions at earlier stages.

In addition, the quoted risks are exaggerated for marinas, commercial harbors, and shipyards because they presume a balanced, diverse, and productive marine community within these sites is an attainable use. Because marinas, for instance, are managed for small boats and may be significant sources of certain pollutants in addition to TBT, it is questionable whether mollusc production, for example, would be a resource management goal and an attainable use. Generally, it is not. In addition, poor hydraulic exchange within marinas affects food supply for filter feeders, and their depositional environment limits habitat, limiting the species that can live in them [36]. Similar constraints on biodiversity occur in shipyards and in the innermost reaches of commercial harbors where we sampled.

Uncertainties in Risk Estimates

There are two categories of uncertainties in our risk estimates: data variability and assumptions. The former includes TBT detection limits. Although our data include absolute TBT quantitative limits as low as 0.5 ng/L, the MDL was 5.5 ng/L, calculated following Federal Register 40 CFR 136, Appendix B. The practical quantification limit for TBT exceeds 10 ng/L using the analytical method of Uhler and Steinhauer [37], which is being adopted as an EPA standard method (A. Uhler, personal communication). As mentioned earlier, EECs less than the MDL were set equal to one-half the MDL. This was inconsequential to the risk estimates, because any value less than the detection limit was associated with zero risk. Because risks resulted from the majority of EECs being at or near one-half the MDL, however, this creates some uncertainty in calculated means. If detection limits were lower, the risks would decline further. This would also be the case if TBT EECs were inflated by noise around the detection limit. Expected improvements in TBT detection limits should reduce this uncertainty.

Assumptions concerning EEC duration and effect thresholds represent important uncertainties. We assumed every EEC occurred long enough to elicit responses in all the species tested, but if they did not, risks were over-estimated. We also assumed exceedance of a species' effect threshold denoted risk, knowing that most thresholds represent estimates of no observed effect concentrations and do not equate with effects. To distinguish effects on individuals and those on populations, further assessment is necessary [38].

SUMMARY AND CONCLUSIONS

Tributyltin monitoring from pre-1989 through 1996 at saltwater and freshwater sites around the U.S. has revealed declines in chronic risks from a high of 25 percent, prior to late 1988 legislation restricting TBT usage, to < 1 to 14 percent in 1996, depending on site type and region. Most of the decline has been associated with marinas, which reflects limitations on use of TBT antifoulant paints on pleasure crafts. Since

1994, all risks have been associated with chronic rather than acute toxicity in all regions monitored. Most of the risks appear to have been localized to marinas (small boat basins). Low risks (≤ 2%) have been observed in commercial harbors and shipyards in three of the four regions monitored for the past five years. Negligible risks (< 1%) have been encountered since prior to 1989 in the fish and shellfish habitats adjacent to marinas, shipyards, and commercial harbors.

Risks were not uniform between regions of the U.S., but were inflated by TBT concentrations measured at a variety of stations within Galveston Bay, which have ranged from 1 - 19%. By 1996, risks were low (≤ 4%) to negligible in the Pacific Northwest (Puget Sound, Washington), Atlantic Northeast (Narragansett Bay,

Rhode Island and Massachusetts), and the Great Lakes (Lake Erie, Ohio, Michigan, and Pennsylvania). Most (86 to 100%) of the aquatic species are not expected to be at risk from TBT surface water concentrations observed in 1996. The species at risk occupy the lower tenth percentile in terms of TBT sensitivity. They include the economically important larvae of bivalves, (*Mercenaria*, *Crassostrea*, and *Ostrea*) and the ecologically important zooplankter *Acartia*. However, these species generally were at risk only in marinas, sites managed for commercial uses rather than shellfish production. Galveston Bay was the exception; the most sensitive species were at risk in marinas, shipyards, and commercial harbors, but not in proximate habitats considered suitable for fish and shellfish production.

Table 1. Example TBT expected risk calculation: saltwater marinas in 1996.

TBT Concentration (ng/L)	Percent EECs in this Range of TBT Concentrations	Percent Taxa Affected [1]	Percent Taxa at Risk
0-5	47	0.041	0.019
6-10	14	5.7	0.80
11-20	23	9.3	2.1
21-30	9.0	13.9	1.3
31-40	3.4	18.2	0.62
41-50	1.3	21.9	0.28
51-60	0.96	25.2	0.24
61-70	0.35	28.5	0.10
71-80	0.31	31.0	0.096
81-90	0.12	33.1	0.04
91-100	0.16	35.6	0.057
101-161	0.15	42.7	0.064
Total Expected Risk			6

EEC = Expected Environmental Concentration.
Percent taxa with chronic effects thresholds occurring within the range of TBT concentrations in the first table column.

Table 2a. Expected chronic risks for all saltwater areas monitored.

Year	Expected Risks (%)			
	Marinas	Shipyards[1]	Harbors	Fish/Shellfish Habitats
Pre-1989	25	-	5	2
1989	12	-	1	1
1990	7	-	0	0
1991	7	-	1	0
1992	8	6	2	0
1993	6	6	3	0
1994	6	5	4	0
1995	5	6	4	2
1996	6	5	6	1

[1] The Navy monitoring stations were classified into the site types used on the EPA-mandated program.
Because shipyards and commercial harbors were indistinguishable, all of the Navy data meeting the harbor designation were considered as such, whether or not they contained a drydock. The EPA-mandated program began in 1992, and shipyards per se were only monitored after this time.

Table 2b. Expected chronic risks for Galveston Bay waters.

| Year | Expected Risks (%) | | | |
	Marinas	Shipyards	Harbors	Fish/Shellfish Habitats
1992	18	15	9	1
1993	19	13	8	1
1994	13	12	10	1
1995	13	13	9	4
1996	13	12	14	1

Table 2c. Expected chronic risks for Narragansett Bay waters.

| Year | Expected Risks (%) | | | |
	Marinas	Shipyards	Harbors	Fish/Shellfish Habitats
1992	2	0	0	0
1993	2	2	0	0
1994	2	1	0	0
1995	3	5	1	1
1996	4	1	1	0

Table 2d. Expected chronic risks for Puget Sound waters.

| Year | Expected Risks (%) | | | |
	Marinas	Shipyards	Harbors	Fish/Shellfish Habitats
1992	9	0	1	0
1993	4	2	3	1
1994	4	1	1	0
1995	3	1	1	1
1996	3	1	2	0

Table 2e. Expected chronic risks for freshwaters (Lake Erie).

| Year | Expected Risks (%) | | | |
	Marinas	Shipyards	Harbors	Fish/Shellfish Habitats
1992	2	0	0	2
1993	2	0	0	0
1994	2	0	0	0
1995	2	0	0	0
1996	2	0	0	0

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An Evaluation of Risks to U.S. Pacific Coast Sea Otters Exposed to Tributyltin[1]

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ABSTRACT

Recent studies have suggested that tributyltin (TBT) and other butyltins may contribute to the deaths of sea otters (*Enhydra lutris*) off the California coast. Although butyltins have been measured in tissues from the dead otters, no cause-and-effect relationship links these tissue residues to the otter deaths. This study assesses potential risks to U.S. Pacific coast sea otters (in California, Washington, and Alaska) from TBT in their diet. We assumed that bivalves serve as the primary food consumed. The study looked specifically at how TBT in the diet would affect the species' ability to fight disease (that is, its immune system response). Because no sea otter-specific TBT toxicity data were available, a TBT immune response endpoint was selected for study in a surrogate mammalian species (with relevant uncertainty factors noted). This endpoint was chosen because effects to the immune system occur at the lowest doses evaluated and because disease has been cited as the greatest cause of death in California sea otters. Next, the potential for risk to sea otters is estimated for individual sea otters within threatened populations, as well as for the subspecies populations of Alaska, Washington, and California as a whole.

Results indicate that no TBT-related risks are expected to any Alaska, Washington, or California sea otters foraging in the coastal waters. These waters represent the habitat where more than 99 percent of the sea otter population is known to reside and forage. A few otters, individuals that have been observed in marinas of Alaska (i.e., Seward, Cordova, and Kodiak) and California (i.e., Monterey Bay area marinas and Morro Bay), may be at risk from TBT exposure if they forage on prey living in the marina. Because the California sea otter population is listed as threatened under the Endangered Species Act, the risks to those individual sea otters using the marina habitat were evaluated using the most conservative scenarios. For example, sea otters were assumed to feed on marina bivalves for 20 to 50 percent of their diet; it was also assumed that all TBT was 100 percent bioavailable. These assumptions probably overestimate risks, (that is, they are very conservative) because these otters are believed to consume more varied prey both inside and outside marinas, and other prey (like crab) may accumulate less TBT in their tissues than do bivalves. Risks are estimated to be negligible to the subspecies populations as a whole, because less than one percent of sea otters in California, Washington, and Alaska frequent marinas.

INTRODUCTION

Three subspecies of sea otters inhabit the Pacific coastal waters of California, Washington and Alaska. Evidence suggests that a few individuals in the California subspecies frequent marinas inside Monterey Harbor and Morro Bay (R. Jameson, 1998 personal communication, B. Hatfield, 1998 personal Communication). Otters have also been observed in marinas in Seward, Cordova, and Kodiak, Alaska (C. Gorbics, 1998 personal communication, C.E. Bowlby 1998 personal communication). Within these marinas, we speculate these otters may feed on crustaceans,

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molluscs, and fisherman bycatch or fish scraps. We have anecdotal evidence that the otters feed on fisherman bycatch or fish scraps. Although the fish scraps are not from fish inhabiting the marinas, other food items of otters, such as molluscs and crustaceans, may inhabit marinas and be preyed upon; therefore, risks to sea otters that obtain a portion of their diet from marinas are assessed.

Butyltins bioaccumulate in some bivalves more readily than in other otter prey items, such as crustaceans and fish (Laughlin 1996), because bivalves cannot metabolize TBT as efficiently as other prey species (Laughlin 1996, Lee 1996). For this reason, sea otters feeding primarily on a diet of bivalves may be at greater risk for TBT exposure than crustacean or fish-eating marine mammals.

We undertook this study to estimate the potential risks of TBT to sea otters inhabiting the coastal waters of Alaska, Washington and California. Specifically, we assessed potential risks to sea otters foraging in areas with high boating activity, versus those foraging in their primary coastal habitat. This coastal habitat would be distant from boating areas but inclusive of harbors and bays. Affecting this study is the 1988 legislation limiting the use of TBT[2] in the U.S. Many studies indicate TBT concentrations in water, sediment and bivalve tissues have been declining since 1988 (Russell et al. 1996, Cardwell et al. 1998, O'Connor 1996, U.S. Navy and U.S. EPA 1997). Because of this decline, we hypothesized that sea otter exposures to TBT have been declining as well. Therefore, risks were assessed using both current and historical TBT data in bivalves. The details of the risk assessment methodology and results are presented below.

METHODS

Exposure Assessment

An exposure assessment identifies the type of TBT exposure that sea otters may experience. This assessment consists of the following processes:

- identify the exposure pathway(s),
- identify the exposure data (expected environmental concentrations) used to estimate risks, and
- quantify the exposure using simple dose models.

Exposure Pathway Identification

Given sea otter foraging habits, we assumed the predominant exposure pathway is through their food. We also assumed that other exposure pathways, such as water and sediment ingestion and dermal contact, contributed insignificantly to total TBT exposure. As discussed earlier, the sea otter diet consists primarily of bivalves (e.g., mussels), sea urchins, abalone, crab and fish (see Table 2). While most of the TBT tissue data for saltwater organisms on the west coast of the United States is derived from mussels, *Mytilus spp* (NOAA Mussel Watch Program 1998, Parametrix, Inc. 1998, Russell et al. 1996, U.S. Navy & U.S. EPA 1997), no TBT tissue data were available for other organisms in the sea otter diet. Mussels, therefore, were assumed to be the representative prey of sea otters. This is a conservative assumption because TBT is known to bioaccumulate to higher levels in bivalves than in other prey (except possibly gastropods) due to the limited ability of these organisms to metabolize and excrete TBT (Laughlin 1996, Lee 1996).

Exposure Data Identification

TBT tissue data sources used to calculate otter TBT doses included the following:

- the National Oceanic and Atmospheric Administration's (NOAA) Mussel Watch Program (downloaded from the NOAA web site),
- the U.S. Navy TBT Monitoring Program (U.S. Navy and U.S. EPA 1997), and
- the U.S. EPA-required TBT long-term monitoring program (referred to herein as LTMP) (Russell et al. 1996, Parametrix, Inc. 1998).

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2 . The Organotin Antifouling Paint Control Act restricted use of TBT-containing paints to certain size vessels and a specific release rate.

NOAA Mussel Watch data are available for the sea otter's range in coastal waters off central California (e.g., Monterey Bay, San Luis Obispo Bay); the northwestern tip of Washington State (Cape Flattery); and for several locations in Alaska (e.g., various sites in Prince William Sound, Kachemak Bay, etc.). The NOAA Mussel Watch Program sites represent coastal areas that sea otters occupy but the sites did not target areas where elevated TBT concentrations are suspected (e.g., marinas). We could not locate site-specific marina bivalve residue data for the sites otters use. Therefore, we used marina data collected in San Diego, California (U.S. Navy and U.S. EPA 1997), and Puget Sound, Washington (Russell et al. 1996, Cardwell et al. 1998) to represent TBT residues that an otter foraging in a boating area may be exposed to through its diet. This is a very conservative approach, and risks are certainly overestimated, because bivalves in U.S. marinas have higher TBT concentrations than those in harbors (Russell et al. 1996, Parametrix, Inc. 1998). Several years of tissue data are available for each of these sources: NOAA data from 1989 – 1996;

Navy data from 1986 – 1992, and LTMP data from 1992 – 1997. As necessary, TBT tissue concentrations were converted to wet weight and expressed as TBT cation.

Because one of the objectives of this risk assessment is to evaluate current risk versus trends in risk over time (for sea otters exposed to TBT), the data were evaluated separately for each year sampled. Only single composite samples were available for the NOAA data for each location for each year sampled. However,

for the Navy and LTMP data, multiple samples were available for each year sampled (e.g., 15). Thus, for the Navy and LTMP data, means were calculated and used in the risk assessment. To evaluate the variability in the NOAA single-point composite sample data (concentrations for each station are from a composite sample of multiple mussels), the data from all of the California locations near sea otter populations were combined (on a yearly basis) to evaluate overall exposures to the California otter population. In Washington State only one NOAA sampling station was monitored; therefore, data from the single station were used to represent Washington coastal waters. For Alaska, we did not make a distinction in the NOAA stations that were located near otter populations because TBT residue data were non-detects at all stations except one.

TBT tissue data used in this study indicate that TBT concentrations tend to be much greater in marinas than in coastal waters (suggesting that TBT contamination is localized to its source), and that tissue concentrations continue to decrease with time. The tissue data represent TBT concentrations from the sea otter's food and are used to estimate TBT doses to otters, as discussed below.

Quantification of Sea Otter Exposures

Sea otter TBT exposure was quantified by estimating the daily dose (mg TBT/kg body weight) that sea otters would receive from ingesting TBT in their food, as shown in equation (1):

$$\text{TBT Dose (mg/kg/d)} = \frac{C_{food} \times IR_{food}}{BW} \tag{1}$$

Where:

C_{food} = TBT concentration in food (mg/kg-wet)

IR_{food} = Food ingestion rate (kg/day-wet)

BW = Sea otter body weight (kg)

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The food ingestion rates and body weights used for California, Washington, and Alaska sea otters appear in Table 5. As explained in detail in the Risk Characterization Methods, TBT doses were assessed using mean TBT tissue data, as well as probabilistically, to address the variability in the TBT tissue concentrations. The mean tissue concentration was used to estimate exposure because over a chronic (i.e., long-term) duration otters will feed on bivalves with both relatively high and relatively low TBT concentrations (i.e., they are unlikely to exclusively feed on just bivalves with high concentrations or just bivalves with low concentrations). Because sea otters are exposed to an average TBT concentration in their food over a chronic duration, variability in the mean concentration was evaluated rather than variability in individual concentrations.

RISK CHARACTERIZATION

Potential risks to sea otters from ingesting TBT in bivalves were estimated using the hazard quotient (HQ) approach, where:

$$\text{Hazard Quotient} = \frac{\text{TBT Dose}}{\text{Toxicity Threshold Value}} \quad (2)$$

Hazard quotients were calculated using single point estimates based on mean or single point TBT tissue data (depending on the data source) and the average of the NOAEL and LOAEL for each immune suppression effect. The average approximates the true toxic threshold dose, which is somewhere between these two values. Hazard quotients were calculated assuming ingestion of 100 percent bivalves from coastal areas (NOAA Mussel Watch data) and assuming 10, 20, 30, or 50 percent of the diet consisted of marina bivalves and the remainder was coastal bivalves.

In addition, hazard quotients were also evaluated probabilistically for California otters to quantitatively assess uncertainty in the dose estimates and in the toxicity threshold values. Uncertainties in the HQs were quantified using the normal distribution of TBT exposure concentrations described in the Exposure Characterization and the uniform distribution of toxic thresholds explained in the Toxicological Effects Characterization. These distributions are inserted into the HQ model shown in Equation 2 above, and Monte Carlo analysis is used to create a distribution of HQs.

Monte Carlo analysis involves running a model (in this case, the HQ model) and repeatedly performing the calculation using randomly selected sets of input values (i.e., TBT tissue concentrations and toxicity thresholds) each time. While the input values are randomly selected, the selection of values is a function of their probability of occurrence. For example, see the normal probability distribution below:

Concentrations (on the horizontal axis) corresponding to the taller part of the curve are more likely to occur than concentrations corresponding to shorter parts of the curve, and concentrations that do not lie below the curve have a probability of occurrence at (or very close to) zero. The model (in this case the HQ calculation) is sampled thousands of times to define the probability distribution of HQs. The probability distribution of HQs can be used to estimate the mean HQ, the upper and lower bound HQs, or the probability of exceeding an HQ of 1.0 (or any other HQ).
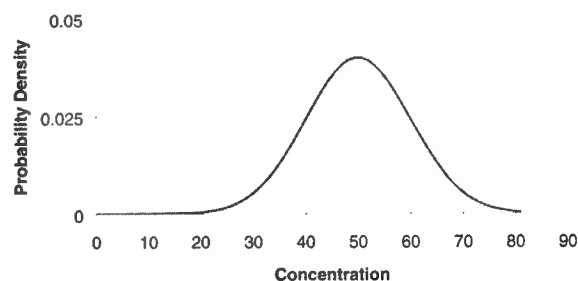
Example of normal probability distribution.

RESULTS

Summary of Results

Overall, current and historical data suggest that sea otters inhabiting the coastal areas of California, Washington, and Alaska ¾ which feed on bivalves, fish, or other invertebrates ¾ are not expected to be at risk from exposures to TBT. Nor are the few sea otters feeding within marinas, which comprise less than 1 percent of the population in California and Alaska, currently at risk from exposure to TBT. This assumes that less than 10 percent of their diet consists of bivalves living in the marina. This finding also assumes sea otters are at least four times more sensitive to TBT than rats.

Potential risks to California sea otters may currently exist if they:

- increase the frequency with which they feed in marinas such that greater than 20 percent of their diet is from within marinas,
- and they feed exclusively on bivalves in the marina,
- and are eight times more sensitive to TBT than a rat (the surrogate test species).

Potential risks to Alaska sea otters may currently exist if they:

- increase the frequency with which they feed in marinas such that greater than 30 percent of their diet is from within marinas,
- and they feed exclusively on bivalves in the marina,
- and are four times more sensitive to TBT than a rat (the surrogate test species).

For sea otters feeding on fisherman's by-catch and prey other than bivalves (e.g., crab), exposures are expected to be lower and may not exceed the toxic threshold dose for immune suppression (based on a moderate decreased resistance to roundworm infections). This is so because, even if the prey is living within the marina, it is expected to metabolize TBT more efficiently than bivalves (Laughlin 1996; Lee 1996), and therefore, accumulate less TBT. No risks are currently expected for any sea otters feeding inside or outside of marinas when TBT intakes are compared to immune suppression endpoints for decreased thymus weight or strong decreased resistance to roundworm and bacterial infections.

Historical marina data suggest potential risks to sea otters, if one assumes they fed exclusively on marina bivalves and that sea otters are four (Alaska) to eight (California) times more sensitive to TBT than the rat.

CONCLUSIONS

Concerns exist that TBT may be posing risks to marine mammals, such as sea otters, off the U.S. Pacific coast. This concern has been raised because TBT

Table 12. Mean and upper and lower bound hazard quotients (HQs) for California sea otters exposed to TBT in marina bivalves collected in 1997.

	Effect Endpoint			
	Moderate Decreased Resistance to Roundworm Infection		Decreased Thymus Weight and Strong Decreased Resistance to Roundworm and Bacteria Infection	
	Males	Females	Males	Females
Bivalve diet from within marinas = 50%				
5th Percentile HQ =	1.62	1.47	0.16	0.15
50th Percentile HQ =	3.13	2.85	0.31	0.28
95th Percentile HQ =	11.88	10.62	1.19	1.08
Probability of Exceeding	100%	100%	5%	5%
Toxic Threshold				
Bivalve diet from within marinas = 30%				
5th Percentile HQ =	1.02	0.91	0.10	0.09
50th Percentile HQ =	1.93	1.75	0.19	0.18

Table 12. Mean and upper and lower bound hazard quotients (HQs) for California sea otters exposed to TBT in marina bivalves collected in 1997.

95th Percentile HQ =	7.40	6.61	0.73	0.07
Probability of Exceeding Toxic Threshold	100%	95%	0%	0%
Bivalve diet from within marinas = 20%				
5th Percentile HQ =	0.69	0.64	0.07	0.06
50th Percentile HQ =	1.33	1.22	0.13	0.12
95th Percentile HQ =	5.05	4.65	0.50	0.46
Probability of Exceeding Toxic Threshold	70%	60%	0%	0%
Bivalve diet from within marinas = 10%				
5th Percentile HQ =	0.40	0.36	0.04	0.04
50th Percentile HQ =	0.74	0.67	0.07	0.07
95th Percentile HQ =	2.83	2.56	0.28	0.25
Probability of Exceeding Toxic Threshold	30%	30%	0%	0%

concentrations have been measured in dead sea otters (Kannan et al. 1998). We evaluated risks from exposure to TBT to the three subpopulations of sea otters in Alaska, Washington, and California. To evaluate the effects of TBT on sea otters, we assumed a diet of bivalves, knowing this would provide a conservative estimate of TBT exposure because bivalves bioaccumulate TBT and cannot metabolize TBT as readily as fish or other invertebrates (Laughlin 1996, Lee 1996). We also calculated risks based on the percentage of the diet coming from bivalves living in the marina (i.e., 50, 30, 20 and 10 percent). Finally, because site-specific data were lacking for Alaska and California marinas, where a few individual sea otters have been observed, marina data from Puget Sound, Washington, and San Diego, California, were used. For all other locations, site-specific data were available through the NOAA Status and Trends Mussel Watch Program.

Immune suppression was the endpoint chosen for this assessment because butyltins are documented as immunosuppressants, and because reproduction is not as sensitive an endpoint. No TBT toxicity data for sea otters could be located; therefore, toxicity data for the rat (surrogate species) were used, with body weight scaling applied to adjust for the difference in metabolism, and with uncertainty factors of four and eight applied, to adjust for the difference in the species being assessed, and whether the sea other population was threatened or not.

In coastal waters, regardless of location or the uncertainty factor applied, all HQs calculated using current data were less than one, the level where a potential for risk is assumed. The only potential risks to otters from TBT exposure were observed in marinas. These risk predictions varied depending on the uncertainty factor used and the percent of diet obtained

in marinas. Overall, risks to Alaska otters frequenting marinas were evident only when greater than 30 percent of the diet consisted of marina bivalves. Risks to California sea otters were evident when greater than 20 percent of their diet consisted of marina bivalves. Risk predictions were also similar between male and female otters. These risk predictions are based on exposures exceeding a moderate immune suppression response. However, when exposure levels were compared to strong immune suppression responses, no risks were predicted for sea otters that may forage in marinas. Finally, risks were negligible to the population as a whole, because less than one percent of California, Washington, and Alaska sea otters frequent marinas.

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Impacts of Invasive Species Introduced through the Shipping Industry – An Overview and the Role of Policy-Makers

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ABSTRACT

Invasive species—also called exotic, nuisance, nonnative, or non-indigenous species—have been introduced inadvertently into many fresh and marine waters by the shipping industry. These species are transported as fouling organisms on ship hulls and in the ballast water and sediments of ships, resulting in the transport of organisms across oceans, as well as between coastal ports. Ballast water samples have included a broad range of species including most trophic levels. While most ship fouling is associated with sessile invertebrates and plants, evidence suggests that mobile species, such as fish, can also accompany a heavily fouled vessel. The degree of fouling on ships, fishing vessels, and private boats has been reduced through the use of antifoulant paints. Prior to their use, about one-third of the introduced species in Australia are believed to have been transported via fouling organisms on the hulls of overseas vessels. Some fouling still occurs today, especially in situations where antifouling paint cover is chipped, difficult to apply, or otherwise ineffective. In addition, ballast water exchange activities continue to introduce non-native species. Invasive species can have adverse ecological and economic impacts by causing declines in native species through habitat alteration or by out-competing native species, and thus, permanently reducing biological diversity. Mariculture and commercial and recreational fishing can also be adversely affected because the new invading species are predators, competitors, and parasites, and some cause or carry disease. Finally, some invasive species, such as toxic dinoflagellates and cholera-causing bacteria, can affect human health as well.

Key Words: invasive species, fouling, ballast water, antifouling

INTRODUCTION

Invasive species have been introduced to new ecosystems by various pathways, a primary one being the shipping industry, both in ballast water and sediment, and on fouled hulls. This type of transport has been referred to as "floating biological islands" (Carlton 1985). Once established, invasive species can cause considerable adverse environmental effects by competing with native species or introducing disease (Williams and Sinderman 1991). They can also cause millions of dollars worth of economic impacts (Carlton and Geller 1993, MDEQ 1999).

The introduction of invasive species is certainly not a new phenomenon. It is expected that invasive species have spread around the world via shipping for the past several centuries. Most likely first on the fouled hulls of wooden ships, then as ballast when hard ballast was replaced with water, and now through both means.   Prior to the use of current day antifoulants, tar and waxes were used to help prevent fouling on wood ships. Later came copper plates, and with the move to steel hulls, antifouling paints containing a variety of chemicals. Some of these chemicals are now well-known for their toxic effects, such as DDT, arsenic, and organomercury (Bennett 1996). Others used metals, such as silver, copper, zinc and tin. Copper

and tributyltin are the predominant compounds in use in antifouling paints for ocean-going vessels today.

Over the 20th century marine transportation has expanded rapidly. Shorter port turn-around times and faster methods of travel have led to an increase in the risk of unintended introductions (Minchin and Sheenan 1995). Ballast water exchange - whereby water (and accompanying organisms) from one location is used as ballast for travel between ports, upon which it is emptied from the ballast tanks to take on cargo, releasing the organisms in the ballast tanks to the new area – is a major source of species introductions. Although ballast water exchange continues to be evaluated by the United Nations International Maritime Organization (IMO), thus far, ballast exchange practices still raise concern. Add to this, a move towards changes in hull antifouling practices from biocides to non-biocidal antifouling methods, and one can expect an ever-greater number of introductions. In addition, changing global environmental conditions may influence species introductions. Introductions may increase if worldwide water temperatures increase due to global warming (Gollasch in prep, Hine 1995).

DISCUSSION

The number of invasive species introductions ranges by region and compatibility of the area. For instance, it is believed that at least 140 species have been introduced to the Great Lakes (US and Canada) (MDEQ 1999). Reise et al. (1999) estimates that 80 species have been introduced to the North Sea. Cohen and Carlton (1995) indicate 253 species have been introduced to San Francisco Bay, California. Introductions are greater in estuaries versus the open coast (Reise et al. 1999).

Carlton and Geller (1993) document 367 taxa present in plankton samples from the ballast water of a ship travelling from Japan to Oregon. Heretofore, ballast water exchange has been considered the primary route of introductions from the shipping industry; however, recent studies indicate that fouled hulls are actually primary contributors (Reise et al. 1999, CSIRO 1999, Rainer 1995, Gollasch in prep), even with todays highly effective antifouling practices in place. At the Marine Corrosions conference in Melbourne, Australia, February 1999, Dr. Minchin (pers. comm.) confirmed that even though TBT-based paints are effective, hull fouling still remains an important problem. He noted that a ban on TBT is likely to lead to further increases of fouling biomass on ships hulls, which will likely lead to an escalation of invasions.

Gollasch (in prep) indicates that in his North Sea study, more than twice as many invasive species were found on fouled hulls than in ballast water. He also found that an average of 14 percent of the hull surface was fouled on the 131 mainly container ships he sampled. These new findings further support that fouled ship hulls are a primary route of invasive species introductions world-wide. Rainer (1995) concludes that prior to the introduction and widespread use of antifouling paints about one-third of the invasive species introduced into Australia came from fouled hulls of overseas trade ships. With the introduction of effective antifouling paints, there has been a reduction of fouled hulls, considerably reducing the risk of invasive organism introductions. Since 1972, the use of antifouling coatings containing TBT has significantly decreased the risk of introductions by fouling organisms. Carlton (1993) also notes that the degree of fouling on ships, fishing vessels, and private boats has been reduced through the use of antifoulant paints, and thus, has reduced the introduction of organisms via ship fouling (CSIRO 1997, Elston 1997). However, despite this reduction, fouling still occurs today, especially in situations where antifouling paint is damaged, difficult to apply, or otherwise ineffective, and as Gollasch (in prep) found, invasive species were present in 98 percent of the 131 hull samples collected and these were

primarily from container ships. In addition, Gollasch also found that the fouling organisms on ship hulls had the highest potential for establishment in new areas.

Recently, with the IMO review of harmful biocides in antifoulants, the pathway of invasive species introductions via ship fouling is being revisited. In fact, at the 1999 Corrosions Conference in Melbourne, Australia, the session on invasive species discussed hull fouling as a primary route of introduction of invasive species. Ships have the unique ability, through both ballast and fouling, to transport a very broad array of organisms to all coastal and inland waterways around the world in a manner the organisms could never achieve on their own.

FACTORS AFFECTING INTRODUCTION

Several factors affect the establishment of invasive species into a new area including environmental tolerance of the invasive species (e.g., to changes in water temperature and salinity), species interactions, food availability, and species competition in the new area. Obviously, the more similar the new area is to their native habitat, the more likely the introduced species will successfully establish. Water temperature and salinity of the potential new area are key in the establishment of species in a new area (Carlton 1985)

Carlton (1987) identified 14 major transoceanic routes and 4 interoceanic routes, with primary receivers (Hawaiian Islands, Australasia, and the Pacific Coast of North America), and donors (Australasia, Japan, and the Indo-Pacific) environments. He notes that donor environments tend to be from continental climates, while receivers have more maritime climates.

Recent data indicates that the use of antifouling paints may be important in preventing the introduction or expansion of invasive species in an area. At the Marine Corrosions conference in

Melbourne, Australia, February 1999, Dr. Minchin (pers. comm.) reported that the spread of zebra mussels (*Dreissena polymorpha*), an introduced species to Ireland, probably from fouled hulls of British boats or Dutch ferries, appeared to be controlled by the presence of TBT. Dr. Minchin believes that a TBT ban will likely lead to an escalation of invasions. He also stated that although TBT is an effective antifoulant, hull fouling remains a problem. Whatever antifouling agents are introduced will need to be as effective or better than TBT to prevent further invasions.

IMPACTS OF HARMFUL INVASIVE SPECIES

Invasive species can potentially constitute a serious ecological, economic and public health problem in any area they successfully colonize. Invasive species may out-compete or change habitats to such an extent that they make it impossible for native species to survive. Development of and/or investment decisions in fisheries and aquaculture may be constrained if invasive species harmful to native and/or cultured species become established in a region. Some invasive species may also affect native species and humans directly by causing illness or even death (e.g., harmful algal blooms and associated biotoxins). Invading species are often predators, competitors or parasites. Some invasive species can cause or carry disease so severe that they can change ecosystems and that a parasite with suitable intermediate host requirements could be spread throughout the world via ships (Williams and Sindermann 1991). Regardless of the direct or indirect nature of the effect, invasive species can significantly affect human health, devastate ecosystem, fishery and aquaculture resources, and severely impact human economy.

The economic impacts of introductions can be severe - in the millions of dollars (U.S). For instance, some of the algae causing harmful algal blooms are thought to have been transported into

new areas in the ballast water of coastal and transoceanic vessels (UNESCO 1991). These represent some of the better known and documented instances of successful invaders causing great harm at a considerable cost. About one fourth of bloom-causing species produce toxins that may harm or kill higher forms of life such as zooplankton, shellfish, fish, birds, marine mammals, and even humans, that feed either directly or indirectly on the algae. In addition, some bloom-causing species do not produce toxins but affect organisms indirectly through other means, such as decreasing light penetration, oxygen depletion, etc.

EXAMPLES OF INVASIVE SPECIES IMPACTS

- The comb jelly (*Mnemiopsis leidyi*), introduced to the Black Sea via the shipping industry in the early 1980s, *now comprises up to 95% of the biomass in the Black Sea* (CSIRO 1998). It feeds on zooplankton, eggs and fish larvae. The comb jelly reduced the anchovy fisheries from hundreds of thousands of tons to tens of thousands; thus, *collapsing a fishery worth US$250 million/year* (Harbison and Volovik 1994).

- The European featherduster worm (*Sabella spallanzanii*) was introduced into Australian waters likely as a fouling organism on ship hulls. The worm forms large mats that smother other sea life and it competes for food with native species. In Port Phillip Bay, near Melbourne, Victoria, Australia *it poses a major threat to the local scallop industry, which is worth an estimated A$15 million annually (~ $11 million/US)* (Bonny 1995).

- The Japanese kelp (*Undaria pinnatifida*) and the Japanese seastar (*Asteria amurensis*) were introduced to Southeastern Australia, Tasmania and New Zealand (kelp only) via the shipping industry. The kelp competes for

space with native marine life and the seastar consumes native shellfish (e.g., abalones). These two species, along with a toxic dinoflagellate (*Gymnodinium catenatum*) *are believed to have cost the shipping, mariculture and fishing industry millions of dollars annually in Australia* (CSIRO 1997).

- The European green crab (*Carcinus maenas*) has been introduced to the east and west coasts of the US, as well as to the waters of Australia, Brazil, Panama and South Africa (Grosholz and Ruiz 1996). Introductions to the US are likely the result of ballast water or from crabs clinging to heavily fouled ship hulls. Green crabs eat molluscs, crustaceans, polychaetes and green algae. They have been *linked to the decline in the scallop fishery in the northeast US and concern for the Dungeness crab fishery on the west coast of the US* (Fincham 1996; Copping and Smith 1998). European, South African and California studies indicate the green crab has the potential to *significantly alter the distribution, density and abundance of prey species, and thus profoundly alter the ecology where it has been introduced*. It has a very diverse diet, can inhabit a broad range of habitats, and it can tolerate a wide range of temperatures and salinities, making it one of the more threatening introduced species to North America. It has been shown to reduce native populations of invertebrates in controlled experiments (Grosholz and Ruiz 1995), and it has reduced populations of bivalves on the east coast of North America (Glude 1955). In 1995, Grosholz and Ruiz predicted that it will significantly affect embayments along western North America, and in only 10 years it has made its way from San Francisco Bay, California where it was first documented in 1989-90, to Washington and British Columbia in 1999.

- The Asian bivalve *Potamocorbula amurensis*, which **changed the structure of the entire food web in San Francisco Bay** (Kimmerer et al. 1994).

- The snail *Littorina litorea* that was introduced to the northern east coast of the US via ship hulls, probably bringing with it the parasite trematode *Cryptocotyle lingua* (Williams and Sindermann 1991). The trematode now has several intermediate hosts along the north Atlantic coast, causing negative alterations in each of their population dynamics.

- Zebra mussel (*Dreissena polymorpha*) in the Great Lakes has been estimated to have a potential economic impact of $5 billion over the next 10 years to industries (water suppliers, power plants, ships and fisheries) in that region (MDEQ 1999).

Several species of invertebrates, plants, and fish have been introduced via the shipping industry, although their economic and ecological impacts may not have been quantified. Some examples of invasive species, with an emphasis on those species introduced via fouled hulls, include the following:

Fish
Japanese sea bass – *Lateolabrax japonicus*

Molluscs
Limpet – *Crepidula fornicata*
Chiton – *Amaurochiton glaucus*
Mussels – *Mytilopsis sallei, Musculista senhousia, Perna canaliculus*
Sea snails/slugs – *Aeolidiella indica, Janolus hyalinus, Okenia plana, Polycera capensis, Godiva quadricolor*

Crustaceans
Barnacles – *Balanus amphitrite, B. improvisus , Elminius modestus, Megabalanus rosa, Megabalanus tintinnabulm*

Crabs – *Carcinus maenas, Eriocheir sinensis, Pyromaia tuberculata, Rhithropanopeus harrisii, Halicarcinus innominatus*
Isopods – *Paracereis sculpta, Paradella dianae, Sphaeroma walkeri, Cilicaea latreillei, Synidotea laevidorsalis, Synidotea laticauda*
Sea Spider – *Ammothea hilgendorfi*

Annelids
Polychaetes (marine worms) – *Boccardia proboscidea, Goniadella gracilis, Hydroides dianthus, H. ezoensis, Janua brasiliensis, Marenzelleria viridis, Pileolaria berkeleyana, Sabella spallanzanii, Ficopomatus enigmaticus*

Echinoderms – (sea star) *Asterias amurensis*

Cnidaria
Sea Anemones – *Haliplanella luciae, Bougainvillia ramosa*
Hydrozoa – *Clavopsella navis, Blackfordia virginica, Gonothyraea clarki*

Ascidians (sea squirts) – *Ciona intestinalis, Ciona savvignyi, Styela clava, Styela plicata*

Sponges – *Halichondria coalita*

Bryozoa – *Shizoporella unicornis, Anguinella palmata, Bugula flabellata, Conopeum tubigerum, Watersipora arcuata*

Parasites
Gut parasite of the mussel *Mytilus edulis* – *Mytilicola intestinalis*
Tremetode *Cryptocotyle lingua* through intermediate snail host (*Littorina littorea)*, which probably was introduced on ship hulls – now also inshore fishes are intermediate hosts

Marine plants – *Solieria chordalis, Undaria pinnatifida, Antithamnionella hilgendorfi*

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If less effective antifouling paints are used and ballast water exchange practices are not controlled and enforced, additional species with similar life histories to those listed above could potentially be introduced via shipping in the future.

Since much of the economic impact caused by invasive species is hard to quantify due to lack of existing data, this topic should be viewed as a potential "economic time bomb." More research on this topic is needed to quantify the potentially disastrous economic consequences of invasive species.

SUMMARY AND CONCLUSIONS

The shipping industry presents a primary pathway for invasive species introductions – both through ballast exchange and through fouled hulls. Both of these topics are currently under discussion by the IMO. In regulating the shipping industry, the IMO should consider both the direct and indirect impacts of its actions in terms of ecological and economic factors. For instance, when considering the control or elimination of all harmful biocides in antifoulant use, it should fully evaluate the ramifications of such a decision. The biocidal nature of antifoulants serve an obvious purpose – to prevent fouling organisms from establishing on ship hulls. They also serve an ancillary purpose, of reducing introductions of invasive species. Because transport of most trophic groups to destinations worldwide can be accomplished either through ballast water or ship hulls, it puts our coastal habitats at great risk. The IMO needs to consider when developing mechanisms to address, control, implement and enforce shipping practices. It would be a shame to potentially have influenced the extent of introductions through one pathway - ballast water exchange - to have it go unnoticed because of the overwhelming effects of another – the control of biocidal antifoulants. Fouled hulls have already been documented as a primary route of introductions despite current antifouling practices. The control of biocidal antifoulants needs to be balanced with the indirect benefits they

provide until an effective non-biocidal alternative is developed.

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Assessing the Impact of Antifouling Compounds in the Marine Environment. Lessons to be Learned From the Use and Misuse of Biological Indicators of TBT Contamination

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ABSTRACT

The condition known as imposex in whelks has been used widely as a biological indicator of tributyltin (TBT) contamination in the marine environment. It has provided valuable information on the extent and impact of contamination. It has also been used successfully in monitoring changes in levels of contamination since regulations, limiting the use of TBT-based antifoulants to vessels >25 m in length, were introduced. However, its misuse has also generated misleading information. There have been at least four reasons for this. First, sampling has been biased on 'hot-spots' of contamination, giving a false impression of the severity of the problem. Second, imposex is not, as has often been assumed, a specific response to TBT. Third, insufficient attention has been given to the longevity and habits of indicator species. Fourth, predictions of extinctions of species, which have been based on assessments of imposex, have not been fulfilled. It is argued that, while biological indicators should play key roles in assessing the impacts of pollutants, rigorous protocols are needed.

I. INTRODUCTION

It is generally accepted the tributyltin (TBT) is the most effective biocide ever used in antifouling paints. TBT-based coatings have been used widely on yachts, mariculture structures and ocean-going vessels. They improve a ship's performance by preventing the growth of fouling organisms on the hull, thereby reducing drag and concomitantly decreasing fuel consumption. This brings, not only enormous savings to the shipping industry, but also environmental benefits. Lower fuel consumption means reduced emissions of 'acid rain' and 'greenhouse' gases. An additional benefit is that effective antifouling prevents the transport of invasive (non-native) organisms on ship hulls. Such organisms can have enormous ecological and economic impacts, and pose major threats to marine ecosystems.

However, the use of TBT also has environmental costs. It leaches from the antifoulants into the water column and can cause damage to non-target organisms. It was, for example, held responsible for the near collapse of oyster farming in west France and for the demise of populations of dogwhelks in areas of high boating activity in southwest England during the 1980s. Not surprisingly, the use of these TBT-based paints was regulated in a number of countries, including Europe, USA, Canada, Australia and New Zealand. Several governments reacted by banning the use of TBT-based coatings on vessels <25m in length.

There is an obvious need to monitor the success of the regulations in reducing levels of TBT. However, there are difficulties in making, and interpreting the results of, chemical measures of TBT in the environment. This is for three reasons. First, TBT can be effective at concentrations which are close to the limits of detection. Second, there are sometimes large spatial and temporal variations in concentrations of TBT at fixed locations because it may be

released into the environment in pulses (e.g. from dry docks) which may be biologically harmful but may be missed by regular sampling. Third, the distribution of TBT in the environment is complex. It occurs at much higher levels in the surface microlayer and sediment than in the water column.

As a result of these difficulties, bioassays have been developed as indicators of TBT contamination. Imposex has been one of these. TBT causes imposex, in which male genitalia, a penis and vas deferens, become superimposed on the female's system. Gibbs *et al.* (1987) recommended two quantitative measures of imposex: (i) the relative penis size index (RPSI) which compares the size of the penis of the female with that of the male as a standard; and (ii) the vas deferens sequence index (VDSI), which recognises six stages primarily in the development of the vas deferens. Females at stages 1 - 4 of the vas deferens sequence (VDSI) are capable of breeding, but those at stages 5 and 6 are rendered sterile. Additional measures of the health and/or reproductive status of populations, suffering from imposex, have been made in some studies. They include assessments of abundance of whelks on the shore, adult sex ratios (populations with male-biased ratios are likely to have suffered from high female mortality) and the proportions of juveniles in populations (as indicators of juvenile recruitment and therefore breeding performance).

II. THE USE OF IMPOSEX AS A BIOLOGICAL INDICATOR OF TBT CONTAMINATION

The first detailed survey of imposex was of the dogwhelk *Nucella lapillus* in southwest England in the mid-1980s. Bryan *et al.* (1986) found that the condition, and presumably therefore TBT contamination, was severe in areas of high boating activity. In the most severe cases, there was female sterility and premature death. There was an absence of juveniles in some populations and, in the worst affected areas, the species became locally extinct. Further surveys showed that the condition was widespread. It was reported in surveys of *N. lapillus* in northeast England, Scotland, the British coast including the Isle of Man, the Netherlands, and the entire coastline of the North Sea. In other whelk species, it occurred in Canada, USA, Malaysia, Singapore, Indonesia, West Africa, New Zealand and Australia (Evans *et al.* 1995).

However, although TBT contamination was severe in the 1980s, regulations which prohibited the use of TBT-based antifoulants on small boats, have been highly successful in reducing ambient concentrations of TBT in the marine environment. Evidence has come from a number of different sources. These include the recovery of populations of oysters

and reduced concentrations of TBT in the water column, sediments and tissues of molluscs. Populations of whelks have shown three clear signs of recovery: reduced symptoms of imposex, increased abundance and fecundity and the recolonisation of some areas where they had become locally extinct.

The current situation is that commercial harbours, especially those with dry-docking and repair facilities, are still hot-spots of TBT contamination. However, the impacts of these remaining hot-spots are surprisingly localised. Gradients of sharply decreasing contamination have been described from dockyards, marinas and commercial harbours in Hong Kong, ports and fishing harbours in Iceland, marinas in Israel and a boatyard on the Isle of Cumbrae, Scotland (Table 1).

Table 1. Gradients of TBT in tissue and imposex (RPSI) in samples of dogwhelks *N. lapillus* across a boatyard entrance at Millport, Scotland.

Distance from boatyard entrance (metres)	TBT (ng/g dry weight)	RPSI
100	65	1.3
75	66	0.5
50	85	0.7
25	109	0.4
entrance (north)	369	12.9
entrance (south)	217	12.1
25	88	0.7
50	59	0.4
75	58	1.1
100	46	0.9

III. THE MISUSE OF IMPOSEX AS A BIOLOGICAL INDICATOR OF TBT CONTAMINATION.

However, there is not full accord. There have been some claims, based on surveys of imposex in whelks, that, despite the regulations, TBT contamination has continued to worsen. According to the North Sea Quality Status Report (1993), TBT pollution of the North Sea is so bad that it is likely to have catastrophic effects on the survival of sensitive species such as the dogwhelk. This assessment is based on an account of a survey by Harding *et al.* (1992) of imposex in *N.lapillus* in coastal areas of the North Sea and English Channel. An additional concern is that the open North Sea is contaminated. Ten Hallers-Tjabbes *et al.* (1994) found imposex in some common whelks *Buccinum undatum* from central and southern parts of the North Sea, and report that its severity correlated with the intensity of shipping in adjacent areas. Cadee *et al.* (1995) predicted that *B. undatum*

would eventually become extinct in the North Sea with the continued use of TBT-based antifoulants.

The results of these studies have been contradicted by more recent work. The predicted catastrophes have not occurred. Both *N. lapillus* and *B. undatum* are still abundant in the North Sea, and symptoms of imposex are generally mild (Evans *et al.* 1996; Nicholson & Evans 1997). However, these findings raise questions about the value of imposex as an indicator of TBT contamination. There appear to be at least four areas of concern:

(i) Biased Sampling. Sampling programmes have concentrated on hot-spots of contamination, such as drydocks, marinas and ports, giving a false impression of global contamination of the open seas and oceans. Where programmes have included areas of open coast adjacent to hot-spots, the impact has been local. Imposex-free populations, or those with mild symptoms, have been described within a few km of pollution at Loch Sween, Scotland, Wellington Harbour and Porirua Inlet, New Zealand, Port Philip Bay, Melbourne and Ambon Bay, Indonesia.

(ii) The Causes of Imposex. Imposex is not, as has often been assumed, entirley specific to TBT. Extensive studies by Bryan *et al.* (1986) appeared to establish that, apart from two related organotins, tri-*n*-propyltin and tetrabutyltin, TBT was the only compound to cause it in *N. lapillus*. The finding that copper, and even environmental stress, could induce it imposex in *Lepsiella vinosa* was therefore unexpected. Subsequently, it has been shown that triphenyltin, nonylphenol and exposure to faeces of seabirds can induce it in different species of whelks (Table 2).

(iii) The Habits of Indicator Species. Since imposex is irreversible, it tends to reflect conditions which have prevailed in the past rather than ambient ones. It is particularly difficult to interpret its significance in *B. undatum*, which is a long-lived, mobile species. It is sensitive to TBT during its juvenile development only. Since it can survive for 15 or more years, imposex may reflect conditions which prevailed a decade and a half previously, at some unknown location.

(iv) The Use of Imposex to Indicate Fecundity. Harding *et al.* (1992) reported that many populations of *N. lapillus* at sampling sites on the coast of Norway were sterile based on assessments of imposex. However, the expected extinctions have not occurred. The species is still common or abundant, and fecund, at these sites (Evans *et al.* 1996).

Table 2. The development of imposex in dogwhelks *N. lapillus* exposed to TBT and nonylphenol in the laboratory.

| | Group | | | |
	TBT controls	TBT	Nonyl-phenol controls	Nonyl-phenol
Sample size	40	40	40	40
Mean VDSI	1.7	3.7	1.9	3.1
Mean RPSI	4.2	15.7	1.4	14.1

IV. CONCLUSIONS

(i) Imposex in whelks is a useful biological indicator of TBT contamination. It can indicate the extent of contamination, its biological impact and can also be used for long-term monitoring of populations of whelks.

(ii) The condition must be used with caution. It can be caused by agents other than TBT so that confirmatory chemical measures are always needed. Care is needed in the design of sampling programmes and in the interpretation of imposex scores.

(iii) While biological indicators of should play key roles in assessing the impacts of pollutants, rigorous protocols are needed.

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An Overview of the Science and Regulation of TBT and the Potential for Future Liability for Contaminated Harbor Sediments

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ABSTRACT

A draft Assembly Resolution prepared by the Marine Environmental Protection Committee (MEPC) of the International Maritime Organization (IMO) to propose a global ban on the use of organotins in antifouling paints was approved by the IMO Assembly at its 21st Regular Session (November 1999). In approving the Resolution, the Assembly agreed that a legally binding instrument (global convention – an international treaty) be developed by the Marine Environment Protection Committee that should ensure by January 1, 2003 a ban on the application of Tributyltin (TBT) based antifouling paints and January 1, 2008 as the last date for having TBT-based antifouling paint on a vessel. The Assembly also agreed that a Diplomatic Conference be held in 2001 to consider the adoption of the international legal instrument. Monitoring, policing, enforcement, fines and record keeping are yet to be defined. In addition, the MEPC has also proposed that IMO promote the use of environmentally safe anti-fouling technologies to replace TBT.

In the U.S., existing coastal zone, federal and state regulations have had a significant impact on reducing TBT levels, generally to well below the provisional water quality standard of 10 ng/L, and in bivalve tissues. Current environmental and marine and estuarine water concentrations are well below predicted acute TBT toxicity levels. Estimation of chronic toxicity effects using mean water TBT concentrations indicate that current levels would be protective of 95% of species. Analysis of allowable Daily Intake/Oral Reference Dose Values from market basket surveys and the NOAA National Status and Trends data suggest that there is no significant human health risk from consuming seafood contaminated with TBT. Most of the data that exceeded these values were from areas of high TBT input from ports, harbors and marinas (commercial shipping, shipyards and drydock facilities) and sites of previous contamination. In the U.S., at this time, TBT environmental data and lack of acceptable alternatives does not justify a global ban for TBT.

This papers presents a discussion of: (1) Global environmental TBT concentrations and exceptions, (2) Comments on the scientific basis for the regulation of TBT, (3) The TBT scientific controversy, (4) Antifouling biocides and invasive species, and (5) The potential liability to shipping industry, shipyards and paint manufactures from the global ban on TBT in antifouling paints.

Keywords: Tributyltin, TBT, biofouling, antifouling marine coating, regulation, policy, toxicity, invasive organisms, liability and contamination of dredged materials.

GLOBAL ENVIRONMENTAL CONCENTRATIONS A DECADE AFTER REGULATION

In the United States, since the passage of the Antifouling Paint Control Act of 1988, the environmental concentrations of organotin compounds have declined (Seligman et al., 1990; Wade et al., 1991; U.S. EPA, 1991; Valkirs et al., 1991 and Huggett et al., 1992). Three national and regional monitoring programs in the U.S. have sampled for TBT since the passage of OAPCA in 1988. These are the U.S. National Oceanic & Atmospheric Administration's

(NOAA) National Status and Trends Monitoring (NS&T) Program, which was created in 1984 (see O'Connor, 1998. Overviews are presented in the Proceedings of the Coastal Zone 93 and the special issue of MPB Vol. 37 No. 1 (O'Connor and Pearce, 1998) and the papers there in. A second TBT monitoring program was the U.S. Navy Long-term Monitoring Program associated with Navy home ports and harbors (See U.S. Navy, and EPA, 1997). The third monitoring program is the consortium of tributyltin manufactures (ORTEPA) Long-term Monitoring Program contracted to Parametrix Inc., with results published in Cardwell et al., (1997; 1999); ORTEPA (1997, 1998). The results of these three national monitoring programs have been compared by Russell et al. (1998) who found that all of these programs have found declining environmental concentrations of TBT over time since the enactment of OAPCA in 1988. Water concentrations have declined 56% - 71%, sediment 47% -55% decline, and bivalve tissues 40%-82% within a few years. Mean TBT concentrations in water are generally below the current U.S. EPA marine chronic water quality criterion of 10 ng/L (Russell et al., 1996).

Studies have found that mean TBT surface water concentrations have significantly decreased in San Diego Bay, following legislative restriction on the use of organotin antifouling paints in California. Regression analysis of the San Diego data suggests that surface water concentrations would decrease by 50% in 8 to 24 months. It was found that sediment TBT concentrations in San Diego Bay did not reflect recent decreases in water column values and were variable among stations over time, and that tissue concentrations in *Mytilus edulis* have generally declined in San Diego Bay since February 1988 (significantly since April and July 1990), Valkirs et al. (1991).

Similar findings have been reported for the Chesapeake Bay by Huggett et al. (1992) for the Hampton, Virginia area of the Bay. Surface water samples analyzed after the passage of the Organotin Antifouling Paint Control Act (OAPCA) of 1988 in marinas and yacht clubs indicated that TBT concentrations had significantly decreased when compared to results of earlier studies by Huggett (1986, 1987) and Huggett et al., (1986), U.S. EPA Chesapeake Bay Program, (1987), and Hall (1986; 1988); Hall et al. (1986; 1987).

The EPA Report to Congress (U.S. EPA, 1996) is a summary of the status of development of alternatives to TBT. The driving force is to develop an alternative to TBT, which could compete in the $ 500 million per year total antifoulant paint market (C&E News, Oct 14, 1996). The TBT copolymer used in deep-ocean going vessels represents between 65-70 percent of this market. The goal is to develop a non-toxic (no effect on non-target organisms) antifoulant, which effectively inhibits the formation of biofilms and prevents biofouling. The major finding of the EPA 1996 Report (which has not been updated) was that "an alternative antifoulant as effective as TBT self polishing copolymer paints has not been found." They also reported that the principal alternatives today to TBT antifouling paints are copper-based. However, hulls treated with copper-based paints were reported to foul within 15 to 18 months due to formation of a "green layer" on the surface of the hull. The green layer is the reaction of copper to seawater, which results in the formation of a coating of insoluble cupric salts, preventing the release of copper from the paint underneath. Once the green layer is present, the antifoulant protection is no longer effective. Underwater hull scrubbing is required to remove the green layer and attached fouling organisms and with frequent scrubbings, the period of protection can be extended for up to 30-36 months depending on water temperatures. Revised estimates on fuel savings from the use of TBT by the Navy ranged from 18 to 22 percent of the total fuel consumption (U.S. EPA, 1996).

EPA has recently noted that noted that the use of copper is coming under increasing regulatory pressure with some coastal states restricting the amount of copper that may be discharged into local harbors during hull cleaning and washing. These regulations may impact the U.S. Navy's use of copper in antifoulant paints and leave the Navy without alternatives that meet their requirements. The Navy has held a workshop on the chemistry, toxicity and bioavailability of copper and its relationship to regulation in the marine environment to improve the scientific understanding of copper in the marine environment and attempt to develop a solid scientific basis for future approaches to copper regulation (Seligman and Zirino, 1998). In addition, the Navy has funded the development of in the water

cleaning systems for copper that also collect all waste and wastewater for treatment (Bohlander & Montemarano, 1997). It also should be noted that both Holland and Sweden have recently introduced regulations on antifouling paints for pleasure vessels containing copper as effective September 1, 1999. Canada has set the release rates of copper in antifouling paints at 40 mg/cm^2/day. Copper is a potential toxin to marine organisms (Lewis and Cave, 1982; and Goldberg, 1992). It should also be noted that the U.S. Department of Defense and the U.S. Environmental Protection Agency have been working on the Uniform National Discharge Standards (UNDS) which will regulate the amount of biocidal discharges from antifouling coatings into the sea by December 2000, with the current release rates under consideration for copper less than the 40 mg/cm^2/day. (see UNDS Website: http://206.5.146.100/n45/doc/unds/SITEMAP/ITEMAP.HTML).

TBT concentrations in water, sediment, and biota have generally declined. Evans (1999b) has an excellent summary paper on the concentrations and environmental effects as a measure of the effectiveness of national regulations. TBT concentrations in surface marine waters have declined in Arcachon Bay, France (Alzieu et al., 1986, 1989) and in the UK (Cleary, 1991; Waite et al., 1991, 1996; Dowson et al., 1992, 1993a, 1993b and 1994) the USA (Valkirs et al., 1991; Huggett et al., 1992, 1996; and Uhler et al., 1993) and in the Gulf of Mexico from Wade et al., 1991; and Champ and Wade, 1996; Garcia-Romera et al., 1993) and Australia (Batley et al., 1992). Tissue concentrations in molluscs have declined (Valkirs et al, 1991; Wade et al., 1991; Champ and Wade, 1996; Waite et al., 1991, 1996; and CEFIC, 1994).

Exceptions to this general decline of TBT in bottom sediments have been reported as hot spots associated with ship channels, ports, harbors, and marinas in Galveston Bay (Wade et al., 1991), Hong Kong (Ko et al., 1995), the Netherlands (Ritsema et al., 1998), Iceland (Svavarsson and Skarphédinsdóttir, 1995) and in Israel (Rilov et al., 1999).

Oyster culture has recovered in France (Alzieu et al., 1986, 1989 and Alzieu, 1991 and 1996). In southern England, Waite et al. (1991; 1996; and Dyrynda, 1992)

reported improved oyster culture. For Australia, Batley et al. (1992) have reported improvements in oysters. Minchin et al. (1987) have reported improvements for scallops and Minchin, (1995) and for flame shells in Ireland.

The literature has also reported wide spread decline in Imposex and population recovery for dogwhelks (*Nucella* spp.): England (Evans et al., 1991; Douglas et al., 1993; Gibbs and Bryan, 1996a 1996b); Scotland (Evans et al., 1994 and 1996; and Nicholson et al., 1998); Ireland (Minchin et al., 1995); Norway (Evans et al., 1996); and Canada (Tester and Ellis, 1995; Tester et al., 1996).

COMMENTS ON THE SCIENTIFIC BASIS FOR THE REGULATION OF TBT

It is interesting to note, that the "movement" to regulate TBT based antifouling paints during the 1980's was initially based on "correlation" and "generality" type science (see Salazar and Champ, 1988). Peruse the bioassay discussions in White and Champ (1984), and see Evans et al. (1996) and Evans (1997 and 1999a; 1999b) for a discussion on Imposex. The Salazar and Champ (1988) paper was a preliminary review of the science that was prepared for an Oceans '88 conference proceedings to stimulate discussions. However, it was published about the same time that OAPCA was passed in the U.S. and interest in TBT and support for further research declined (Champ and Seligman 1996a). Fortunately this was not true on a global basis. Some of these concerns have been revisited and are discussed in a collection of papers reprinted and submitted by the paint industry to the MEPC by the Organotin Environmental Program Association (ORTEP, 1996, 1997 and 1998). Many of these points were discussed at the 1998 Annual Meeting of the American Chemical Society in Dallas (Rouhi, 1998) and in Champ (1998). In addition, papers were presented at the Oceans '99 Conference in Seattle (September, 1999) that discussed the science being used in the regulatory process (see Brancato and MacLellan, 1999; Cardwell et al., 1999; Damodaran et al., 1999; Evans, 1999c; Evans and Nicholson, 1999; Evans and Smith, 1999; MacLellan et al., 1999; and Toll et al., 1999). Several of these papers delineate problems with data quality and quantity, protocols and question the emphasis of the data and the information that is being utilized as a basis

for proposed additional regulation. *However, these points are moot if comparable and environmentally friendly alternatives to TBT are available and acceptable (Champ, 1998, 2000).*

The Scientific Controversy

Early concern was expressed that most of the evidence the regulatory process considered to be significant came from bivalve mollusks: (1) it was believed that mollusks were more sensitive than other animal groups to TBT, (2) Many bivalves have a cosmopolitan distribution and are commonly maintained in the laboratory, (3) filter-feeding bivalves may be more susceptible to TBT due to their feeding strategy, and (4) many bivalves have an economic importance in the commercial shellfish industry (Champ and Seligman, 1999b; 1999c). A significant and subtle distinction that needs to be kept in mind is the difference between the environmental impact of TBT on the shellfish industry and the environmental impact of TBT on natural shellfish populations. The point is that the effects on cultured shellfish do not necessarily demonstrate similar ecological effects in a typical natural situation. A second point is related to public definition of "acceptable" land use. It is difficult to appreciate being interested in culturing shellfish in areas adjacent to marinas and shipyards given their history of being defined as "polluted" due to acute and chronic contamination problems (Champ, 1983). Ports, harbors, and marinas are publicly approved marine land uses. These facilities are usually located in highly protected areas with low flushing rates, long water mass retention times, oil spills, high levels of contaminants, and high silt loads which are not optimum conditions for culturing filter-feeding bivalves.

In Europe, the critical evidence for the initial regulations in the mid 80's, was associated with shell thickening in oysters (*Crassostrea gigas*) and imposex in dog-whelks (*Nucella lapillus*). In the U.S., the early critical evidence was associated with laboratory studies that reportedly demonstrated unacceptable effects on growth and development in oysters (*C. gigas, Ostrea edulis*) and clams (*Mercenaria*) (Champ, 1986). All of this evidence was based on only four species, a similar number of laboratory tests and field observations, generally unsupported by chemical measurements and not published in peer reviewed journals. In general, the laboratory studies utilized questionable methodology and field studies lacked the necessary scientific rigor.

Bioaccumulation of TBT from Sediments

In what may become a classic regulatory textbook debate and case study, are the results of a 5-year study of TBT-contaminated sediments associated with an U.S. EPA Superfund site in Washington State. The issues unresolved are summarized in a U.S. EPA Region 10 Technical Memorandum (for addressing unanswered questions) that is entitled: "Topics Related to the Tributyltin Study at the Harbor Island Superfund Site, Seattle, Washington" (Keeley, 1999, Personal Communication). During EPA Superfund remedial investigations at the Harbor Island Site (Weston, 1994), TBT had been previously identified as a contaminant of potential concern due to elevated concentrations in the marine sediment (higher concentrations ranged from 10 to 50 ppm dw TBT).

Because there are no established Federal or State sediment quality guidelines or standards for evaluating TBT concentrations in sediment, the U.S. EPA formed an interagency working group to identify and evaluate approaches to deriving an effects-based sediment cleanup concentration for use at Superfund sites in Puget Sound, Washington. Most of the available literature presented toxicity of TBT for water, and only two studies (covering four species) evaluated toxicity associated with sediment concentrations of TBT (U.S. EPA, 1996a). The working group also proposed the calculation of an Apparent Effects Threshold (AET) value, which could be used as a sediment criteria for TBT, using available chemical (bulk sediment) and biological (sediment toxicity, benthic infauna) data from Puget Sound. The working group found that: (1) Existing Puget Sound data did not support a clear identification of an AET value for TBT; (2) A maximum no-effect concentration could often not be established because, in several cases, the highest sediment TBT concentration was associated with no biological effects and was also the highest concentration measured among all the stations sampled; (3) Good correlations were <u>not</u> found between bulk TBT sediment concentrations and laboratory toxicity and *in situ* benthic community responses; and

(4) Based on an evaluation of available information, "bulk sediment concentrations of TBT were a poor predictor of bioavailable TBT" (U.S. EPA 1996a). Further, the working group recommended, based on a general understanding of chemical partitioning and the lack of observed relationships between bulk sediment TBT and adverse ecological effects, that when TBT is a contaminant of concern in sediment, pore water concentrations of TBT should be measured, and toxicity testing or bioaccumulation testing (*in situ* or laboratory) be conducted to confirm the ecological significance of concentrations measured in pore water. The working group did not provide recommendations for specific bioaccumulation test species, because it was believed that additional work needed to identify the most appropriate species (ESI, 1999a).

In a series of subsequent TBT related studies, a consortium of Harbor Island waterfront property owners (the Port of Seattle, Lockheed Martin Corporation and Todd Shipyards Corporation) funded a study to evaluate the bioavailability of and the potential effects associated with TBT in sediments at the Superfund site. The overall purpose of this study was to develop a site-specific, effects-based TBT tissue trigger concentration that could be used to determine the need for remediation of TBT-contaminated sediments. In this study, effects considered relevant for the development of a site-specific tissue trigger value were mortality; reduced growth; and reproductive impairment. The normal TBT effects cited in the literature, such as bivalve shell thickening or induction of (early stage) imposex or intersex in meso- and neogastropods, were not appropriate in this evaluation, because (1) these biological responses do not have established connection to population-level effects, and (2) there is a lack of suitable habitat at the site for the species (oysters, mesogastropods, and neogastropods) typically affected by shell thickening, imposex and intersex. The study site is a deep (-30 to -60 ft mean lower low water), industrialized channel of subtidal sediments within the Duwamish River Estuary. Very little intertidal habitat is available, due to extensive channelization and dredging of the waterway, and no commercial or recreational shellfish beds occur. In addition, gastropods typically are not a large component of the benthic community at the site, and mesogastropods and neogastropods are very limited in abundance (ESI 1999a). The study was performed

in accordance with a Sampling and Analysis Plan (SAP), prepared by ESI (1998) that was reviewed and commented on by all reviewers prior to its approval by U.S. EPA, and resultant data from the TBT study were determined to be of high quality by EPA (ESI, 1999b).

The evaluation of TBT sediments from the Harbor Island sediments was conducted in two studies. First, a TBT literature review was conducted to identify global paired tissue residue and effects data for marine invertebrates and fish (ESI 1999a). The tissue residue data were used to estimate a site-specific, effects-based tissue trigger concentration for TBT (ESI 1999a). Second, sediment samples were collected throughout the study site for chemical and biological testing (ESI 1999b). TBT concentrations were measured in bulk sediments and pore water samples; a subset of sediment samples collected was used for bioaccumulation testing. With approval from all involved agencies and consistent with national guidance, bioaccumulation testing was conducted to determine site-specific exposures to two marine invertebrate species: (1) a bivalve (*Macoma nasuta*) and (2) a polychaete (*Nephtys caecoides*). No approved marine sediment toxicity bioassay protocols for test species that have demonstrated sensitivity to TBT were available (U.S. EPA, 1996a), so no toxicity testing was conducted. The resulting tissue TBT concentrations were then compared to the effects-based trigger concentration derived from the literature (ESI 1999b; Keeley, Personal Communication).

Results of this study were that the survival of the laboratory test organisms was high, and the lipid content of the organisms exposed to test sediments was similar to controls, which suggest to many of the projects reviewers that the organisms were in good physiological health during the exposure period. A site-specific tissue trigger (3 mg/kg DW TBT) was estimated (Meador, 2000) for the study site for evaluating bioaccumulation data from the study area, and for the 20 stations sampled and tested at the site, none of the tissue samples from the bioaccumulation tests exceeded the tissue trigger value of 3 mg/kg DW TBT. Thus, no cleanup of TBT sediments was recommended. The value of 3 mg/kg DW TBT, which was derived from paired tissue residue effects data in the literature, is estimated to be the tissue residue

associated with reduced growth in a number of invertebrate species. The level is however, very similar to the overall geometric mean of paired effect/no-effect data and the estimate of a sublethal effects level based on a multi-species acute-to-chronic effects ratio for the study area.

The development of tissue residue effects thresholds is part of EPA's overall strategy for management of specific contaminants in sediments in the US rivers and estuaries. The lack of TBT bioaccumulation from sediments in these studies is not understood, creating more unanswered questions and confusion in the data and suggests that further studies are needed prior to the development of a protocol for estimating TBT tissue level triggers for regulatory use. Results from the study also found that TBT tissue concentrations were most strongly correlated with dw-sediment and carbon-normalized sediment TBT concentrations, and there were weak correlations with filtered and unfiltered pore water TBT concentrations. If there is no relationship between levels in sediments and bioaccumulation levels in tissues, then the TBT in the sediments has been shown to not be bioavailable. For the determination of ocean dumping for dredged materials, the decision has to do with whether a species has accumulated more than 3 mg/kg DW TBT.

After completing the Harbor Island TBT bioaccumulation studies, the U.S. EPA (1999) prepared a Technical Memorandum to address topics of interest identified by EPA and other agency reviewers on issues related to the findings presented in the above study (ESI, 1999c). Several scientists reviewing the results of the Harbor Island studies had a difference of opinion in the interpretation of the results. Some reviewers of ESI (1999b) indicated that the measured TBT bioaccumulation in test organisms for this project was less than they would have expected from the measured sediment and pore water TBT concentrations in site samples. This concern was based in part on a comparison of the bioaccumulation test results with studies reported in the literature and with other similar studies performed in the general Harbor Island area. Some reviewers suggested that several test parameters (e.g., species selection, exposure regime of tests, organism health) might have influenced the results.

Salazar and Salazar (1999a, b, in preparation) in reviewing the Harbor Island bioaccumulation studies believe that the major lesson learned from this study and their separately conducted caged bivalve bioaccumulation studies are that lab tests don't predict nature very well, or adequately consider equilibrium and energetics. They have listed the following specific lessons learned from their research on TBT uptake by mussels that: (1) Lab tests generally over-estimate toxicity; (2) Lab tests generally under-estimate bioaccumulation; (3) Bivalves are sensitive test species; (4) Exposure period should be determined by equilibrium; (5) Growth rate affects bioaccumulation potential; (6) Quantifying health is important in data interpretation; and (7) Tissue chemistry can be used to predict effects. Salazar and Salazar (1987; 1989; 1996) and Salazar et al. (1987) have found that survival and growth effects of TBT were over-estimated based on laboratory tests and mesocosm studies. They placed caged mussels at the seawater intake to test tanks and found that growth rates were about 4 times faster outside the test tanks compared to growth in the control tanks.

In the Harbor Island studies, the issue is the interpretation of the tissue chemistry data and Salazar and Salazar (1996a b, in preparation) believe that, even though the U.S. EPA followed all state and national guidance and accepted state-of-the-art testing protocols, they believe that laboratory exposures have under-estimated bioaccumulation levels due to animal health from test conditions. Meador (Personal Communication) suggests that *Macoma* in these tests were more than likely ventilating clean overlying water, reducing its exposure to TBT. Generally speaking, bivalves are extremely sensitive to food and flow rate and growth rates seldom if ever achieve the growth rates of animals in nature. Laughlin (1996) reported that BCF is related to growth rate and that the highest growth rates were associated with the highest BCFs. Laughlin referred to this as the concentration dependence of TBT accumulation. Widdows et al, (1990) found that the operative mechanism is that growth rate is also related to filtration rate. Laughlin (1996) measured BCFs of only about 5,000 compared to an average of about 30,000 from Salazar (1989); and Salazar and Salazar (1996) transplanted mussels, suggesting that Laughlin's animals may have been under severe stress.

The 28 day exposure bioaccumulation tests in the Puget Sound Studies with the marine bivalve *Macoma nasuta* (which is a facultative feeder – both filter feeding and deposit feeder) did not reach steady state, when the test was extended to 45 days, and the results may have reflected test conditions in which *Macoma* may have been stressed. Originally, EPA proposed modifying the test procedure in accordance with Test Sediment Renewal (EPA Guidance Manual on Bedded Sediment Bioaccumulation Tests (EPA/600/R-93/183) which recommends complete sediment renewal for test longer than 28 days. Bruce Boese (EPA Newport Laboratory and an author of the manual) suggests that the primary reason for performing sediment renewal was to give the animals more "food". For the Harbor Island tests, it was decided to add 0.5 cm of sediment to the test chambers every 7 to 10 days for the entire test (overlaps weekends). Questioned in the study was also the use of lipid content at the beginning and end of the test was considered as an endpoint to evaluate potential stress on the test organisms. Boese (Personal Communication) felt that lipid content of Macoma does not give you any information about the health of Macoma, and that loss/gain of lipids is primarily related to reproduction.

Laboratory bioassays have become an environmental test industry and big business in making regulatory decisions. Their simplicity, cost and reproducibility are very attractive to regulatory policy and decision-makers. However, their scientific value or merit has been repetitively questioned. White and Champ (1983) addressed this issue of "The Great Bioassay Hoax" and Salazar (1986) asked similar questions regarding the application of traditional laboratory toxicity tests to assessments of TBT. Salazar and Salazar have raised these questions to a higher level of sophistication but the old problems still remain. Scientists in the bioassay testing business hesitate to challenge an accepted regulatory test, because of a lack of a replacement, and the process to get one accepted, but still need to strive to develop standardized tests that validate and represent what an organism actually experiences in the environment.

Salazar and Salazar (1999a, b, in preparation) also feel that the other interesting issue here is that they believe that the *Macoma* bioaccumulation test may be flawed for the following reasons: (1) since the ASTM protocols do not require any effects measurements, one can never be sure of the health of the test organisms, (2) the largest and slowest-growing animals generally have the lowest tissue concentrations in transplant studies, and (3) people tend to forget that Macoma is a facultative deposit feeder, and can either filter- or deposit-feed. Recent summary papers have reported that many benthic invertebrates are quite plastic in their feeding mode and readily shift back and forth from filter- to deposit-feeding depending on local environmental conditions and available food and can select between clean and filtered seawater and highly contaminated sediment.

Langston and Burt (in preparation) found that concentrations in tissues of *Scrobicularia plana* (a deposit feeding clam) in the UK reached equilibrium in tissues after 40 days of exposure. They also reported that sediments are an important vector for TBT uptake in deposit-feeding clams. They also concluded that it is particulate rather than desorbed TBT, which is most significant. Laughlin (1996) reports that bioaccumulation factors appear to be high, but field studies, in particular, have not necessarily carefully characterized the route of uptake (water or food).

Salazar and Salazar (1999) have found numerous examples where bivalves have been the most sensitive test species. Their predicted tissue burden for effects in mussels is an order of magnitude lower than that for amphipods based on the work of Meador (1997 and references cited there in) and others. Theory suggests that tissue concentrations for effects should be relatively constant across species and that appears to be true for particular endpoints like growth. The problem is that it is relatively difficult to measure growth rate in an amphipod. The difference in sensitivity is due to the growth rate endpoint in bivalves and the mortality endpoint in amphipods which theory suggests is about an order of magnitude different (McCarty, 1991; McCarty and Mackay, 1993). An additional problem with most laboratory tests is that they were not originally selected and standardized by equilibrium kinetics and steady state.

Amphipod tests are routinely conducted for only 10 days, even though Meador (1997, 2000) has found that it takes about 45 days to reach chemical equilibrium or steady state. This may explain why there appears to

be a disconnect between sediment chemistry, laboratory toxicity tests, and benthic community assemblages using the sediment quality triad. This has led to suggestions of using tissue chemistry to predict effects (McCarty, 1991; McCarty and Mackay, 1993). Subsequently Salazar and Salazar (1991; 1998; and Submitted) developed the exposure-dose-response triad that relies on tissue chemistry to make the link between the various effects endpoints. This relates to Salazar's point of growth rate affecting bioaccumulation potential. Sick and dying animals do not accumulate much TBT, which is why it is essential to confirm the health of the test animals.

With TBT data, they have been able to predict where effects will occur based on where the relationship between water or sediment and tissue TBT begins to change. This was first demonstrated in a graph published in Salazar and Salazar (1996) that plotted the relationship between water and tissue TBT. They found that grouping the data above 105 ng/L gave one regression and at 105 ng/L or lower that it gave a very different regression. The Salazar's recently replotted the Langston and Burt (1991) data and found exactly the same relationship, which Langston concurred. With Langston and Burt's data, they found effects in *Scrobicularia* to occur between 0.1 to 0.3 ug/g TBT dry weight in sediment, which agrees with Meador's data for effects on the polychaete *Armandia brevis* (Meador and Rice, In Press). The Salazar's summarized their findings in a paper presented at the SETAC (1999) meeting in Philadelphia. This paper is being expanded to emphasize the significance of field data over laboratory data in predicting effects and will be submitted to the Journal of Marine Environmental Research. They concluded that these data sets: (1) supports their hypothesis that one can predict the concentrations where effects will begin to occur based on the relationship between external concentrations and tissue burdens; (2) demonstrates that the concept may work for both water and tissue; and (3) suggests that tissue burdens associated with effects (acute 10X > chronic) are relatively constant across marine organisms.

ANTIFOULING BIOCIDES AND INVASIVE SPECIES

Recent research has suggested that hull biofouling will likely play a much greater role in introduction of invasive (exotic) species following a global ban on the use of TBT in antifouling paints. The 10[th] International Congress on Marine Corrosion and Fouling (February, 1999) in Melbourne Australia, included two special sessions on invasive species transported on vessel hulls. Stephan Gollasch, from the Institute for Marine Sciences in Germany gave a keynote address on the importance of ship hull fouling as a vector of species introductions into the North Sea. Dan Minchin presented a paper on data and information from Ireland and Mary Sue Brancato presented data from the U.S. (see also Brancato and MacLellan, 1999). Historically invasive species from the hulls of ships has been mostly an exotic marine algae and plants problem due to the speed and size of ships and water quality in ports.

Minchin estimated that 1.8 million marine organisms could exist on the hull of a severely biofouled vessel (Minchin, Personal Communication). However, after the introduction and use of TBT in the early 70's, fouling on hulls was not considered a significant source problem for invasive species, because in general hulls were cleaner. Considering the coincidence of global climate fluctuations and the proposed global ban on the use of TBT, invasion of species via the biofouling community on fouled hulls of ships may eventually constitute a greater threat then those in ballast water (Minchin and Sheehan, 1999).

Minchin is also concerned that there is a correlation between ship hull hitchhikers and water temperature changes. Ships pass through rapid water temperature fluctuations while entering harbors and channels and ports from the open ocean. These sudden temperature swings may initiate spawning triggering invasive species introduction in ports and port channels. Populations could easily become established in the invaded U.S. port because the U.S. Clean Water Act has greatly cleaned up (reduced pollution) U.S. ports

over the years. In the past, the level of contamination in most ports has reduced the probability of the invading organism becoming established.. With the movement to clean up ports and harbors world wide, the risk of introduction has greatly increased. Minchin believes that IMO must have available replacements that are as effective as TBT, in providing the same degree of protection to coastal waters from invasive species as TBT has for the past three decades. To ban it, we would face serious introduction of invasive species in the temperate environments. Their environmental impacts include changes in biodiversity, food webs, trophic levels competition, and the introduction of disease organisms and parasites.

It has been estimated that over 6000 species have been introduced in the U.S. The introduction of the lamprey eel and zebra mussel in the Great Lakes are examples of major invasive species that have had significant impact on U.S. aquatic ecosystems. The zebra mussel has had detrimental effects on lakeside piers, industrial facilities and public beaches. Another example the European Green Crab (*Carcinus maenas*) has the potential to impact the $20 million dollar crab industry in the State of Washington alone (Brancato, 1999). Additional examples of invasive species are the Toxic Japanese dinoflagellates and the Northern Pacific sea star, which have infested New Zealand and Australia. The American comb jellyfish has greatly impacted the anchovy industry in the Black Sea.

In his keynote address at the 10th International Congress on marine Corrosion and Fouling, Stephan Gollasch reported on historical studies of invasive species in the North and Baltic Seas and compared vectors of introduction including ballast water and hull fouling from 200 ships. In the 1992 to 1995 time frame, Gollasch reported that most of the non-native species with the highest potential for establishment were from fouled hulls, with 53% of the marine exotic species found in the North Sea introduced by shipping and 98% of the hulls sampled revealed non-native species (Reise et al., 1999). Of the species connectable to shipping, 66% were introduced from the hull, 34% from ballast tanks. Gollasch, the second author of Reise et al. (1999) paper is also a scientific advisor and member of the German delegation for the ballast water working group at IMO's MEPC 43. He believes that IMO should consider the hull fouling dilemma in its assessment of the ban of TBT and balance the risk of introduction of invasive species harming local ecosystems with the environmental risks of TBT on non-target species in their decision-making process. He has found that most of the species of high concern are transported in ballast water including cholera bacteria and phytoplankton algae causing harmful algal blooms, but he believes the risk of species introduction from ships hulls is increasing and without TBT it could be even worse (Gollasch, 1999, personnel communication).

TBT CONTAMINATION OF SEDIMENTS IN PORTS AND HARBORS

If TBT is banned by international treaty as proposed by MEPC 42, the future cost of removal of dredged material from harbors and waterways will probably increase significantly. An example of how regulation can increase disposal of dredged material costs is seen in the two alternatives available to the Port of NY/NJ for immediate disposal of dredge spoils. The Mud Dump Site (located 3 miles offshore in the open waters at the mouth of the harbor) has been operational for many decades and has been the traditional disposal area and can accept Category I dredged materials. Category II and III contaminated "spoils" have to be disposed of at an upland hazardous waste disposal facility, however, from 1977 to 1991, 90% of all NY/NJ dredge spoils were tested and classified Category I and only 1 to 2 % were Category III. However, in 1991 the US EPA replaced the existing tests in the NY region and added new bioassay testing which altered Category I, II, and III determinations.

For Category II and III dredged material, the currently available alternative is upland disposal at a hazardous materials storage facility and none are available in the near vicinity. Howland Hook Terminal in Staten Island shipped 150,000 yd^3 of sediment via barge and rail to Utah at a cost of $17 million or over $110/yd^3. Traditional fees for dumping dredge materials at the Mud Dump Site are in the area of $10/yd^3.

If TBT ("as perhaps the most toxic substance ever deliberately introduced to the marine environment by mankind") is banned by an international convention (it will be the first chemical by name to have its own convention or treaty) it could then be considered equal

or more hazardous than Category III compounds. As such it might greatly increase the cost of disposal of dredged materials from most ports and harbors that are contaminated with TBT, because of its persistence and its universal distribution in bottom sediments of ports and ship channels.

An additional concern for the paint companies, shipyards and shipping industry may be that in the future that they have bear the liability for cost contained dredging. It may be that the liability for the additional or special costs of dredging and disposal of TBT contaminated dredged materials from ports and ship channels might revert back in the courts to sources such as have the costs of health settlements from smoking in the courts. The impact on TBT contamination in port sediments on future shipping and port development is significant, for example, plans to dredge the Tyne in Newcastle (UK) may be abandoned, because of extremely high TBT concentrations in the river sediments, and the concern that organotins will desorb form particles on agitation during dredging and disposal of dredge material at sea (Mark G.J. Hartl, Personal Communication). Approval for dredging is pending on the outcome of a survey being conducted by CEFAS, Burnham On Crouch.

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The Effects of Regulating the Use of TBT-Based Antifouling Paints on TBT Contamination

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ABSTRACT

There was severe TBT pollution is coastal waters in the mid-1980s, particularly in areas of high shipping and mariculture activity. Organotin concentrations were high in water samples, sediments and tissues of marine molluscs. Responses, such as imposex in whelks and shell growth abnormalities in oysters, which can be caused by TBT, were also well-developed. They were associated with reproductive failure, and even local extinction of species, in the most severe cases. However, several governments have regulated the use of TBT-based antifouling paints, prohibiting their application to vessels <25m in length. These regulations have been highly successful in reducing TBT pollution. Environmental concentrations of TBT have decreased, and there has been substantial recovery of populations of whelks and oysters. Serious TBT contamination is now restricted largely to ports and harbours, especially those with dry-docking facilities.

I. INTRODUCTION

Tributyltin (TBT) leaches into the marine environment from the antifouling paints which are used on the hulls of boats and mariculture cages. It is potentially highly toxic at low concentrations. This is reflected in low lethal dose (LD) concentrations to TBT in sea water, especially in the case of larvae of invertebrates. For example, the 15day LC50 for larvae of the common mussel *Mytilus edulis* is 0.1 ug/l. However, sub-lethal impacts occur at even lower concentrations. No Observed Effect Concentrations (NOEC) for the growth and reproduction of plankton are 0.4 ng/l, and for shell calcification in oysters and normal development of the genital system in female dogwhelks, 2 ng/l.

TBT has a short residence time of days only in the water column but it becomes adsorbed on to particles and aggregates in sediments, where its half-life may be a matter of years.

There was widespread use of TBT-based antifoulants by the 1980s, and the worst contaminated areas were semi-enclosed bodies of water, which have poor flushing characteristics and in which there was intensive shipping (or ship-related) activity or mariculture. The concentrations recorded in 'hot-spots', such as harbours, marinas, dry docks, estuaries, sealochs and bays, were often well above NOECs. For example, concentrations in the water column were mostly >100 ng/l but occasionally exceeded 300 ng/l (Batley 1996).

Not surprisingly, TBT pollution had impacts on marine biota. The best documented example is from Arcachon Bay (west France), which is a centre for both yachting and oyster culture. TBT leaching from the antifouling paints used on yachts was held responsible for abnormal shell growth and reproductive failure of oysters. Production of oysters fell to about 33-50 % of the normal harvest (Table 1). A similar collapse of oyster farming was reported in estuaries in southern England, and TBT was the probable cause of declines in populations of other bivalve molluscs.

TBT was also linked to declines in populations of dogwhelks *Nucella lapillus* in areas of high boating activity in southwest England (Bryan *et al.* 1986). Female *N. lapillus* developed the condition known as imposex in which male characterisitcs, including a penis and vas deferens, become superimposed on the female's own genitalia. It can cause sterility because the vas deferens becomes convoluted and forms a nodule which blocks the genital pore. As a consequence, the species became locally extinct in Plymouth Sound and in the estuaries of the rivers Dart and Fal.

Subsequently, advanced symptoms of imposex were recorded in *N. lapillus* at other North Atlantic sites, and in other whelk species in Canada, New Zealand, Australia, Japan, Indonesia, Malaysia, Hong Kong, Singapore, the Malacca Strait, Thailand, Israel, Malta, the Mediterranean Sea, Ghana and the Canary Islands. TBT contamination was a widespread problem (Ellis and Pattisina 1980).

Table 1. Production of oysters in Arcachon Bay, France.

Period	Production (tons)
1978-79	10000
1979-80	6000
1980-81	3000
1981-82	5000
1982-83	8000
1983-84	12000
1984-85	12000

II. MANAGING TBT POLLUTION: THE EFFECTIVENESS OF REGULATIONS.

Basically two approaches have been used to reduce TBT pollution. One of these was to ban the use of TBT-based antifoulants on small pleasure craft which were believed to be the main source of contamination in coastal waters. The other approach was to regulate the paints themselves. This was done by, for example, encouraging the use of new copolymer sef-polishing paints, which have relatively slow TBT release rates, and discouraging the use of the original free association paints, from which TBT leaches more rapidly. France was the first to introduce regulations. It did so in 1982, very much in response to the oyster farming problem in Arcachon Bay. The use of TBT-based antifoulants was prohibited on vessels <25m in length. Similar regulations followed in the UK, USA, Canada, New Zealand, Australia, South Africa, Hong Kong and most European countries.

There is substantial evidence that these regulations have been effective in reducing TBT contamination and the adverse effects of pollution. Reductions are due primarily to lower inputs from small boats, and declining levels of pollution have therefore been most marked in estuaries and areas where there are marinas. This has almost certainly been the cause of declining levels in water samples, sediments and the tissues of molluscs. They have been reported in studies worldwide (Table 2).

Table 2. Examples of studies in which reductions in TBT contamination have been described, based on chemical measures.

Location	Reference
UK	Dixon 1989 Cleary 1991 Bryan & Gibbs 1996
Gulf of Mexico	Wade *et al.* 1991
Australia	Batley *et al.* 1992
USA	Wuertz *et al.* 1991
France	Alzieu 1996
Japan, Europe and USA	CEFIC 1994

Concomitantly, there have been recoveries of many of the populations of molluscs which were severely impacted in the 1980s. These have sometimes been dramatic. Oyster farming in France recovered almost immediately after the introduction of regulations in 1982 (Table 1), and oyster farming in England and Australia also improved rapidly following the regulations in these countries. In addition, there has been widespread recovery of populations of other bivalves and gastropods (Table 3).

Table 3. Examples of studies in which recoveries of populations of molluscs have been described, since the introduction of regulations limiting the use of TBT-based antifoulants.

Species	Location	Reference
Dogwhelks	Clyde Sea North Sea	Evans *et al.* 1996
Dogwhelks	Canada	Tester *et al.* 1996
Dogwhelks	New Zealand	Smith 1996
Mud snails	USA	Curtis 1998
Oysters	France	Alzieu 1996
Oysters	Australia	Batley *et al.* 1992
Scallops	Ireland	Minchin *et al.* 1987
Flame shells	Ireland	Minchin 1995

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A recent (1998) survey of imposex in dogwhelks *N. lapillus* along North Sea coastlines illustrates the extent to which recovery has occurred. It was reported that in 1991 there was either total or partial sterility in two thirds of the populations surveyed from Norway, Denmark, the Netherlands, France and the UK (Harding *et al.* 1992). Widespread extinctions might have been predicted. However, the species was present on all of the shores which were revisited in 1998, and it was common or abundant on most of them. Symptoms of imposex had declined, and they were reproducing successfully (Table 4).

Table 4. Measures of imposex (RPSI and VDSI) in North Sea dogwhelks sampled in 1991 and 1998.

	Survey	
	1991	1998
	Norway and Denmark	
Number sites	21	12
Mean RPSI	38	19
Mean VDSI	4.5	3.6
	France	
Number sites	16	18
Mean RPSI	18	6
Mean VDSI	3.9	3.3
	United Kingdom	
Number sites	20	15
Mean RPSI	16	8
Mean VDSI	3.7	3.3

Commercial harbours, especially those with shipyards and dry docks, remain contaminated by TBT. This is because ocean-going vessels continue to use TBT-based antifoulants, and consequently it continues to accumulate in harbour sediments. However, there is evidence of recovery of populations of dogwhelks *N. lapillus* in Sullom Voe (Scotland) where the only source of TBT is from tankers which visit the oil terminal there. It can probably be attributed to the widespread use of copolymer coatings, replacing free association paints.

III. THE FUTURE OF TBT-BASED ANTIFOULANTS: MANAGEMENT OR BAN ?

It is unfortunate that a full understanding of the effectiveness of regulations in managing environmental levels of TBT is becoming apparent only at a time when the International Maritime Organisation (IMO) is considering the introduction of a total ban on TBT-based antifoulants. It is currently considering draft regulations whereby the application of TBT-based coatings will be banned from 2003, and TBT paints (from previous applications) will not be allowed on hulls from 2008.

TBT-based paints have achieved a notoriety which is not justified by the scientific evidence. Furthermore, there is no doubt that additonal regulations could reduce ambient levels of TBT still further. There could, for example, be stricter controls for paint application and removal procedures, dockyard waste disposal and the use and availability of paints. Research is also needed to create new technologies for the treatment of TBT-contaminated waste water, more efficient and less toxic paints and offshore ports where the dilution of open waters will reduce pollution.

The ultimate objective must be to veto the use of all toxins in the marine environment and the use of TBT, or other biocides, should eventually be outlawed. However, there are increasing concerns that the proposed ban on TBT-based antifoulants is premature. A ban will mean the the immediate introduction of alternatives. However, the long-term biocidal properties of alternatives are largely untested, and it is difficult to predict either the economic or environmental consequences of using them. Poor antifouling performance will certainly be costly for the shipping industry because it will result in higher fuel consumption and the need to slip and repaint vessels more often. There may also be environmental consequences. Increased fuel consumption will lead to an increase in emissions of 'greenhouse' and 'acid rain' gases. In addition, the inceased spread of those 'invasive' (non-native) species, which are carried on the hulls of fouled ships, is likely to become a major problem. They already cause enormous ecological and economic damage, and could become the cause on an enviromental disaster. There is a need, furthermore, to demonstrate the alternatives are actually more 'environmentally friendly' than TBT. It is claimed that one alternative, the herbicide booster Irgarol 1051, which is already in use, is at environmental levels which are sufficient to damage phytoplankton communities. Several alternatives contain high levels of copper, and inceased copper content of oysters in Arcachon Bay has been linked with the increased use of such paints, following the ban of TBT-based paints on small boats.

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The Environment: Our Joint Responsibility

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ABSTRACT

It is argued that the environment belongs to all of us and that local communities should therefore be involved in environmental planning processes. It will require increased understanding and awareness of scientific issues in members of the public, and the development of mechanisms by which they can contribute effectively to them. Environmental education in the formal system has been disappointingly ineffective in promoting a scientifically-literate society, and it is suggested that new initiatives, such as programmes of life-long learning and the involvement of community groups in science, are needed to achieve this goal.

Community groups have traditionally managed the local environment, and there is no reason why they and other interested parties, including scientists, industrialists, members of ENGOs and politicians, should not collaborate in its management in the modern world. It will be necessary, however, to accept that 'practical solutions to human needs may require compromise between conflicting priorities'. Global issues will require a different approach but representatives from all groups in society should still be involved. One possibility is to establish advisory panels, which would address specific issues.

INTRODUCTION

The World Conservation Strategy (1980) points out that the behaviour of society as a whole must be transformed in order to develop a new conservation ethic in which humankind is prepared to live in harmony with the natural world. It recognises that lack of awareness and understanding of environmental issues in decision-makers and the general public impede this. It is argued that ecosystems are being destroyed because people do not realise that it is in their best interests to preserve them.

The concept of 'ownership' of the environment is also poorly developed in modern society. Environmental planning is seen by most of us as a distant responsibility, often involving acrimonious confrontation, between scientists, industrialists, planners, statutory bodies, 'green' environmentalists and politicians. In fact, the environment belongs, not to particular sections of society, but to all of us. It follows that a new ethic should embrace the concept that we have a joint responsibility for its future. We should all therefore have the opportunity to contribute to environmental planning processes.

However, this goal can be achieved only if: (i) ways are found of creating a society which is more scientifically-literate; and (ii) mechanisms are developed by which lay members of the community can collaborate with those with special expertise in developing strategies for sustainable use of the environment.

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Awareness and Understanding of Science

The formal education system is an obvious way in which knowledge and awareness, of science can be achieved, and there has been substantially more emphasis on some of its aspects, such as man's impact on the environment, during the past two or three decades. Many schemes have highly laudable objectives. Key Stage 4 of the National School's Curriculum in England and Wales aims to produce pupils who 'form balanced judgements about some of the major environmental issues facing society' and 'recognise that practical solutions to human needs may require compromise between competing priorities'.

Regrettably however, formal programmes appear to have had insignificant impact. There is little evidence of change since Holdren & Ehrlich's (1971) reference to the 'monumental failure of biological education' in influencing the opinions of politicians and industrialists on environmental issues. Evidence that the British adult population has modest knowledge only of simple biological topics (Lucas, 1987), criticisms of school curricula for failing to address 'real' problems (Evans, 1988) and calls for further developments in environmental education (Lakin & Burch, 1996) reinforce the view that there is still much to be done.

Industrial and scientific progress is, in any case, too rapid for the formal education system to be the sole means by which society can keep abreast of new developments. It could be argued that it is the responsibility of industrialists and scientists themselves to keep the public and decision-makers up to date with their findings. Unfortunately, this does not happen. Industrialists have difficulties in getting their messages across because the public perception of industry is of an exploiter (sometimes a ruthless one) of the environment.

However, times are changing rapidly and there is increasing evidence of an enlightened approach, in which industry, government and the community engage in open debate within a climate of mutual trust (Pearce, 1991). Scientists are probably viewed less cynically by the public than industrialists but they are notoriously bad communicators and are often portrayed unsympathetically by the media (Gray, 1999).

A compounding problem is that science has difficulty in reacting quickly to new issues because the publication of research is a slow process, due to dependence on the peer review system to maintain quality. Furthermore, since the journals in which it does eventually appear are unlikely to be read by the public, it falls largely on specialist publications, such as *New Scientist* and *Scientific American*, to present accounts of new developments and balanced views of current issues.

With the paucity of scientific information getting through to the public, the Environmental Non-Governmental Organizations (ENGOs), have enormous power to influence public opinion on major issues. In some respects they use it responsibly. In particular, ENGOs provide an excellent service in drawing the public's attention to matters of concern.

For example, World Wide Fund for Nature (WWF) has been highly successfully in emphasising pollution problems in specific geographical areas, such as Antarctica (Anon., 1981), the Arctic (Anon., 1998) and the Baltic Sea (Ambrose, 1995), in identifying habitats which are endangered, such as Spanish wetlands (Anon., 1999), and in recognising threats to particular groups of organisms, such as sharks (Ambrose, 1998).

Similarly, campaigns by the Marine Conservation Society and the Keep Tidy Britain Group have highlighted problems of plastic litter pollution in the marine environment and water quality on leisure beaches in Britain (Marine Conservation Society, 1991, Anon., 1995). Greenpeace has also

raised awareness of a range of issues, such as whaling, shipments of nuclear waste and problems associated with dismantling oilrigs, often through a more confrontational approach.

ENGOs could also play major roles in disseminating scientific information and to some extent they do so through, for example, the publication of books, such as the Marine Conservation Society's *Good Beach Guide* (1991) and its marine field guide (Hawkins and Jones, 1992), and Greenpeace's publications on the Mediterranean Sea (Pastor, 1991) and Baltic Sea (Leithe-Eriksen, 1992). However, ENGOs often become involved in campaigns and, in these cases, the dissemination of information is less satisfactory. ENGOs, not unreasonably in many ways, use selected data to support their arguments and frequently over-simplify issues.

For instance, the Greenpeace 1996 campaign against Danish fishermen who were trawling for sandeels was based on the simple message: industrial fishing is harmful to the environment and unnecessary, and should be banned. Whether this conclusion is right or wrong, the regulators had to consider the problem from other perspectives. Some influential scientific opinion did not agree with Greenpeace that the fishery was having such a severe impact on the environment, and it also became evident that natural climatic factors may have been responsible, at least in part, for declines in populations of sandeels.

There were social, economic and political considerations because, not only was the fishery of economic importance to Denmark, but Danish access to sandeel stocks had been permitted as a trade-off for the cod and haddock quotas given to other EU member states (Gray *et al.*, in press).

ENGO campaigns against tributyltin (TBT) have been conducted in a similar way. TBT is the active biocide in the antifouling paints, which are applied to boat hulls. It is highly toxic, and therefore an extremely effective antifoulant, but it has caused environmental damage by leaching from paints into the water column (de Mora, 1996). WWF's campaign has been to call for the earliest possible ban on the use of TBT-based antifoulants.

Their case is presented in two brochures, which are part of the *Living Seas* campaign: *Organotin Paints Commercially Used on the Hulls of Ships to Prevent Fouling by Marine Plants and animals are Toxic* and *The Accumulation and Impact of Organotins on Marine Mammals, Seabirds and Fish for Human Consumption* (WWF, 1999). Again, the complexities of the issue are ignored. There is, for instance, overwhelming evidence that regulations prohibiting the use of TBT-based coatings on small vessels and developments in paint technology have minimised the problem so that serious TBT contamination is now limited to commercial harbours and dry docks (Evans, 1999). There is also failure to acknowledge the part played by effective antifoulants in reducing emissions of greenhouse gases due to lower fuel consumption and preventing the spread of 'invasive species' across the world's oceans.

Even more importantly, WWF materials make no reference to concerns among scientists that the environmental profiles of alternative paints, which will be used once TBT has been banned, are poorly known (Stewart, 1996). They could be more environmentally damaging than TBT. Thus, while there is consensus among scientists, and even the chemical industry, that TBT-based paints must eventually be banned, there is serious concern about the timing of the ban. Like almost all economic versus environmental issues, informed choices between alternatives have to be made (Evans and Leksono, 1995).

We must search for non-toxic antifoulants (and there is a real chance that 'non-stick surfaces' based on silicon elastomer technology will be available in the future) but, until superior alternatives are available, we must either tolerate

some pollution from their use, or accept the economic and environmental costs of doing without them. Society as a whole should decide whether some environmental damage, in this case to communities on rocky shores near ports and other centres of boat use (which are already highly perturbed environments), is an acceptable price to pay for the benefits gained from the world's shipping industry and a cleaner atmosphere.

There is an obvious need for new educational initiatives, which will, not only raise standards of scientific literacy, but also encourage more critical evaluation of information. Equally, there are needs to promote increased feelings of ownership and responsibility towards the environment in lay members of the community, and therefore a willingness to contribute to environmental planning processes.

Adult (life-long) learning is one relatively unexploited opportunity, and Thomas (1993) cites an example of the way in which participants at an adult education course used newly acquired knowledge to persuade a farmer to conserve an area of ancient woodland. Schemes involving children of school age and adults (e.g. their parents) can also be profitable. It is taken for granted that the older, hopefully wiser, members of society instruct the younger ones. However, information transfer can occur in the reverse direction.

Evans *et al.* (1996) provide evidence that knowledge of recycling waste materials, which was gained by children at school, was transferred to their parents, and influenced their attitudes towards recycling. One initiative is the Marine Conservation Society's 'Adopt a Beach' Programme (MCF, 19xx).

Another initiative, which aims to forge a closer link between the local community and the environment, is operated by the Department of Marine Sciences and Coastal Management,

Newcastle University (UK) at its Dove Marine Laboratory. Members of the community take part in scientific exercises under the guidance of experts from industry or academia. Participants are expected to produce environmental action plans, which are based, at least in part, on their findings. Projects include assessments of TBT contamination of the North Sea, sustainable bait collection by anglers, marine biodiversity, the bycatch in the local *Nephrops* fishery, and programmes for monitoring shorebirds. The TBT project has shown that, contrary to common belief, dogwhelks *Nucella lapillus*, which were said to be seriously impacted by TBT in the North Sea (North Sea Quality Status Report (1993), are abundant there.

It has generated interest through the media (e.g. Garfield, 1999, Pearce, 1999, Tinsley, 1999) and may therefore have had an impact on the current debate within the International Maritime Organization (IMO) on the need to ban (or regulate further) TBT-based antifoulants.

Joint Responsibility and Collaboration.

The confrontational approach is unlikely to produce effective long-term solutions to environmental problems. There is no doubt that, given the opportunity, all sections of society are capable of working together in partnership. ENGOs worked impressively with Government at the Earth Summit in Rio in 1992 (Rawcliffe, 1998). There, four ENGOs, Friends of the Earth, Campaign for the Protection of Rural England, Royal Society for the Protection of Birds (RSPB) and WWF, became actively involved in the UK Government's roundtable on sustainable development.

Furthermore, RSPB, WWF and the Wildlife Trust are members of its biodiversity working groups. There are also many examples in which these, and other ENGOs, have worked with local government in producing local biodiversity action plans.

There have also been impressive partnerships between ENGOs and industry. WWF, together with other ENGOs and representatives from the timber and retail industries, founded the Forestry Stewardship Council in 1993 (Rawcliffe, 1998). The proposal was to eco-label timber products from those sections of the industry which were prepared to manage their forests sustainably, thereby giving them a competitive advantage. By 1996, 25% of forest products sold in Britain conformed to the eco-labelling criteria. At this time, WWF also founded the Marine Stewardship Council in conjunction with Unilever to ensure that marketed fish were from sustainable fisheries.

Even more recently, WWF has been working with paint and chemical manufacturers in making comparative tests of antifouling paints. Such tests must by their nature take time because TBT-based coatings can provide effective antifouling cover for five or more years. Nevertheless, the discovery of alternative tin-free paint systems, which are shown on full environmental and economic analyses, to be less harmful to the environment than TBT-based paints, is one of the bases on which regulatory decisions should be made.

Unfortunately however, collaboration has not yet replaced confrontation. The position of at least some ENGOs is ambivalent. Greenpeace worked successfully with industry in producing and marketing an 'ozone-friendly' refrigerator *Greenfreeze* (Rose, 1997) but is prepared to take direct action against other sections of industry. Gray (in press) expresses doubt that, despite claims to the contrary, there has been increased collaboration between the ENGOs and industry during the past decade. So why does confrontation occur?

It is a sad reflection if, as Eyerman & Jamison (1998) have suggested, direct actions by ENGOs are necessary to maintain the membership bases. Members of local communities too can play their parts in environmental planning. Indeed, their involvement in them is not a new concept at all. The traditional management of coastal fisheries has, for example, been community-based in many parts of the world. These communities had real or perceived ownership of the area in which they fished, and controlled access to it (Ruddle, 1994).

Such systems have tended to collapse in modern times, due predominately to western influences (Johannes, 1978), but they are still practised in remote regions, such as parts of western Africa (Gordon, 1989) and the Maluku Province in Indonesia (Evans *et al.,* 1997). Ruddle (1988) has suggested that there is much to be learned from them, and that it would be of great benefit if the best of modern management practices could be blended with the best of their traditional counterparts in developing cost-effective management strategies for coastal fisheries.

The proposal is supported by evidence that community-based management can work in the modern world. There have been significant improvements in reef quality, and fish diversity and abundance, on Apo, Negros, Pamilacan and Balicasag islands in the Philippines, following the introduction of a community-based system of management (White & Savina, 1987).

The importance of the community approach to fisheries management, in the sense of involving fishermen in the decision-making processes, has also been recognised in other parts of the Philippines (Pomeroy and Pido, 1994), Denmark (Nielsen, 1994) and Japan (Lim *et a,* 1995).

However, while it is feasible to involve communities in planning processes, which affect the local or regional environment, it is unrealistic to expect their participation in global regulatory processes. There is nevertheless the same need for informed debate, which is unhindered by misleading or unbalanced information. Equally, there is a need for representation from all sections of society.

One way of doing this would be through the establishment of panels whose members would review the available data and make recommendations to the relevant world regulatory authorities. The proposal therefore has much in common with Champ's (1999) suggestion that IMO should form a Marine Coatings Board to consider the TBT issue. It would be expected to expedite the process of creating data and information on which the development and comparative evaluation (including standardised testing) of antifoulants could be made. Champ suggests that it might be a private-public partnership between industry, government and academia but there is still a place for the well-informed non-expert to provide an unbiased input, or perhaps to chair, such a panel.

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14. ABSTRACT

The papers in this Oceans '99 Proceedings Volume represent a global update and state-of-the-art on the treatment of regulated discharges from shipyards and drydocks. The panel discussion identified a series of major concerns or issues from the papers presented that became recommendations for further consideration by interested parties, be they governments (local, regional or national), the shipping industry, the shipyard industry, port and harbor authorities or NGOs such as environmental organizations.

15. SUBJECT TERMS

Characterization of Discharges, Discharge Permits, Regulation, Tributyltin, TBT, Cu, Waste Treatment Systems, Shipyards, Drydocks, Ship Washdown and Shipyard Wastewaters, Storm Runoff, Modeling, Environmental Fate and Effects, Bioaccumulation of TBT, Risk, Contamination, Marine Mammals, Surface Waters, Bottom Sediments, Costs, Solid Wastes

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